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Palladium– and Copper–Catalyzed Amination of Halogenophenyl Substituted Porphyrins for the Synthesis of Porphyrin–Azacrown Ethers Conjugates and Evaluation of Their Sensing Properties

Alexei A. Yakushev,[a] Alexei D. Averin,[a,b@] Olga A. Maloshitskaya,[b] Sergei A. Syrbu,[c] Oskar I. Koifman,[c] and Irina P. Beletskaya[a,c]

Dedicated to Academician of Russian Academy of Sciences Oleg. G. Sinyashin on the occasion of his 60th Birthday

[a]*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, 119991 Moscow, Russian Federation*
[b]*Lomonosov Moscow State University, Department of Chemistry, 119991 Moscow, Russian Federation*
[c]*Ivanovo State University of Chemistry and Technology, 153000 Ivanovo, Russian Federation*
[@]*Corresponding author E-mail: alexaveron@yandex.ru*

The Pd^0- and Cu^I-catalyzed amination of meso-(halogenophenyl)substituted porphyrins and their Zn complexes with propane-1,3-diamine and trioxadiamine was carried out to produce mono- and diaminated derivatives. Conditions for the synthesis of bis- and trismacrocyclic porphyrin-azacrown conjugates with trimethylenediamine linkers via Pd^0-catalyzed amination reactions were established. The properties of two polymacrocyclic compounds to serve as colorimetric and fluorescent sensors for metal cations were investigated, and trismacrocyclic ligand possessing two 1-aza-18-crown-6 moieties arranged symmetrically around the porphyrin core was found to be selective for Cu^{II} in the presence of other metals by strong emission quenching caused by copper ions.

Keywords: Macrocycles, amination, Pd catalysis, Cu catalysis, porphyrins, azacrown ethers, conjugates, chemosensor.

Палладий– и медь–катализируемое аминирование галогенфенил замещенных порфиринов в синтезе конъюгатов порфиринов с азакраун–эфирами и оценка их свойств как детекторов

А. А. Якушев,[a] А. Д. Аверин,[a,b@] О. А. Малошицкая,[b] С. А. Сырбу,[c] О. И. Койфман,[c] И. П. Белецкая[a,c]

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[a]*Институт физической химии и электрохимии им. А.Н. Фрумкина, 119991 Москва, Россия*
[b]*Московский государственный университет им. М.В. Ломоносова, Химический факультет, 119991 Москва, Россия*
[c]*Ивановский государственный химико-технологический университет, 153000 Иваново, Россия*
[@]*E-mail: alexaveron@yandex.ru*

Pd^0- и Cu^I-катализируемое аминирование мезо-(галогенфенил) замещенных порфиринов и их цинковых комплексов с пропан-1,3-диамином и триоксадиамином привело к получению моно- и диаминопроизводных. Найдены условия синтеза бис- и трисмакроциклических конъюгатов с триметилендиаминовыми линкерами с использованием реакций Pd^0-катализируемого аминирования. Исследованы свойства двух полимакроциклических производных

для колориметрического и флуориметрического определения катионов металлов, обнаружено, что трисмакроциклический лиганд с порфириновым двумя фрагментами 1-аза-18-краун-6 эфира, симметрично расположенными вокруг порфиринового ядра, селективен в отношении катионов Cu^{II} в присутствии остальных металлов, и указанные ионы избирательно и полностью гасят флуоресценцию данного лиганда.

Ключевые слова: Макроциклы, аминирование, Pd катализ, Cu катализ, порфирины, азакраун-эфиры, конъюгаты, хемосенсоры на ионы металлов.

Introduction

Modification of porphyrins using catalytic approaches is well documented in literature.[1] For example, *meso*-halogenophenyl substituted porphyrins are known to participate in the Pd^0-mediated amination reactions.[2] Much more extensive catalytic transformations have been described for *meso*-halogenosubstituted porphyrins: amination,[3,4] alkoxylation and aryloxylation,[5,6] sulfonylation,[7] and phosphorylation.[8] The formation of carbon-carbon bonds *via* Suzuki, Sonogashira and Heck reactions are the powerful tools for various modifications of porphyrins[9-11] and construction of di- and triporphyrin systems of various architectures.[12-20] All these reactions were accomplished using Pd catalysis. As for copper-mediated reactions in porphyrins transformation, the majority of literature data deals with "click" reactions which give a lot of possibilities of porphyrins modifications.[21-24] However, in other transformations copper plays a humble role; for example its application was described for the catalytic tetraarylation of *meso*-tetrakis(4-aminophenyl) porphyrin with 4-iodoanisole,[25] CuCl was employed for the synthesis of an awesome square-shaped π-conjugated porphyrin tetramer with diacetylene linkers,[26] $Cu(OAc)_2$ was used in the synthesis of dibutadiyne-bridged porphyrin macrotricyclic dimer.[27]

Recently some of us have studied the amination of mono- and bis(bromophenyl)porphyrins using diamines with secondary amino groups like 1,2-dimethylethane-1,2-diamine (DMEDA) and piperazine,[28] these compounds have been used for the synthesis of porphyrin dyads and triads of various architecture.[29] Copper-mediated famous "click" reactions were also used in the synthesis of porphyrin trimers.[30] In the present work we studied various approaches using Pd- and Cu-catalyzed amination reactions for conjugating porphyrin moiety with azacrown ethers, macrocyclic and macrobicyclic compounds in view of the synthesis of hybrid polymacrocyclic systems – novel polytopic ligands able to bind different metal cations.

Experimental

NMR spectra were registered using Bruker Avance 400 spectrometer, MALDI-TOF spectra were obtained with Bruker Autoflex II spectrometer using 1,8,9-trihydroxyanthracene as matrix and PEGs as internal standards. Propane-1,3-diamine, dioxa- and trioxadiamines, azacrown ethers, 2-(isobutyryl) cyclohexanone, BINAP, DavePhos, cesium carbonate, sodium *tert*-butoxide, CuI were purchased from Sigma-Aldrich and used without further purification, $Pd(dba)_2$ was synthesized according to the method described,[31] halogenophenylsubstituted porphyrines and their Zn complexes **1**, **2**, **9–12** were synthesized according to a described procedure,[32] synthesis of 3-bromobenzyl derivatives of azacrown ethers **23** and **24** and preparation of diamino derivatives of benzylazacrown ethers **25** and **26** were carried out according to a known method.[33] Dioxane was distilled over NaOH followed by the distillation over sodium under argon, acetonitrile was distilled over CaH_2, DMF, dichloromethane and methanol were used freshly distilled.

Porphyrin ***5***. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with porphyrin **1** (0.11 mmol, 83 mg), trioxadiamine **4** (0.33 mmol, 73 mg), $Pd(dba)_2$ (5 mg, 8 mol %), BINAP (6 mg, 9 mol %), absolute dioxane (2 ml) and ^{t}BuONa (0.2 mmol, 20 mg). The reaction mixture was refluxed for 24 hrs, cooled to ambient temperature, diluted with CH_2Cl_2 (5 ml), the residue was filtered off, washed with CH_2Cl_2 (5 ml), combined organic fractions were evaporated *in vacuo*, and chromatographed on silica gel using a gradient of eluents: CH_2Cl_2 – CH_2Cl_2/MeOH 3:1 – CH_2Cl_2/MeOH/NH_3aq 100:20:1–10:14:1. The target compound was eluted with CH_2Cl_2/MeOH/NH_3aq 100:20:3. Yield 16 mg (16 %), deep-red solid. Mass spectrum (MALDI TOF) *m/z*: 890.4753 $[M]^+$. $C_{52}H_{70}N_6O_3Zn$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 0.98 (6H, t, ^3J=7.3 Hz), 1.55 (4H, sextet, ^3J=7.4 Hz), 1.75 (4H, quintet, ^3J=7.3 Hz), 1.90 (2H, br.s), 1.99 (2H, quintet, ^3J=5.6 Hz), 2.27 (4H, quintet, ^3J=7.5 Hz), 2.52 (6H, s), 3.20 (2H, br.s), 3.39 (2H, br.s), 3.47 (6H, s), 3.49–3.60 (8H, m), 3.56 (6H, s), 3.62 (2H, br.s), 3.68 (2H, t, ^3J=5.4 Hz), 3.96 (4H, t, ^3J=7.3 Hz), 7.04 (2H, d, $^3J_{obs}$=8.2 Hz), 7.72 (2H, d, $^3J_{obs}$=8.2 Hz), 9.81 (1H, s), 9.96 (2H, s), NH protons were not assigned.

Porphyrin ***6***. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with porphyrin **2** (0.15 mmol, 120 mg), propane-1,3-diamine (**3**) (0.45 mmol, 33 mg), CuI (3 mg, 10 mol %), 2-(isobutyryl) cyclohexanone (6 mg, 20 mol %), DMF (1 ml) and Cs_2CO_3 (0.225 mmol, 75 mg). The reaction mixture was stirred at 110 °C for 24 hrs, cooled to ambient temperature, diluted with CH_2Cl_2 (5 ml), the residue was filtered off, washed with CH_2Cl_2 (5 ml), combined organic fractions were evaporated *in vacuo* to produce compound **6**. Yield: 55 mg (50 %), deep-red solid. Mass spectrum (MALDI TOF) *m/z*: 744.3803 $[M]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 0.98 (6H, br.s), 1.55 (4H, br.s), 1.71 (4H, br.s), 2.03 (2H, br.s), 2.30 (4H, br.s), 2.45 (6H, br.s), 2.57 (2H, br.s), 3.48–3.58 (14H, br.m), 6.34 (1H, br.s), 6.70 (1H, br.s), 7.20 (1H, br.s), 7.35 (H, br.s), NH protons were not assigned.

Porphyrin 7. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with porphyrin **2** (0.15 mmol, 120 mg), trioxadiamine **4** (0.3 mmol, 66 mg), CuI (3 mg, 10 mol %), 2-(isobutyryl)cyclohexanone (6 mg, 20 mol %), DMF (1 ml) and Cs_2CO_3 (0.225 mmol, 75 mg). The reaction mixture was stirred at 110 °C for 24 hrs, cooled to ambient temperature, diluted with CH_2Cl_2 (5 ml), the residue was filtered off, washed with CH_2Cl_2 (5 ml), combined organic fractions were evaporated *in vacuo* and chromatographed on silica gel using a gradient of eluents: CH_2Cl_2 – CH_2Cl_2/MeOH 3:1. The target compound was eluted with CH_2Cl_2/MeOH 3:1. Yield: 14 mg (10 %), deep-red solid. Mass spectrum (MALDI TOF) *m/z*: 890.4865 $[M]^+$. $C_{52}H_{70}N_6O_3Zn$. ^{1}H NMR (MHz, $CDCl_3$, 298 K) δ_H ppm: 0.96 (6H, t, ^3J=7.3 Hz), 1.55 (4H, sextet, ^3J=7.1 Hz), 1.67–1.78 (6H, m), 1.95 (2H, quintet, ^3J=5.9 Hz), 2.28 (4H, quintet, ^3J=7.2 Hz), 2.60

(6H, s), 2.91 (2H, br.s), 3.17 (2H, br.s), 3.23 (2H, q, ^3J=6.1 Hz), 3.38–3.64 (8H, m), 3.52 (6H, s), 3.58 (6H, s), 3.66 (2H, br.s), 3.96–4.04 (4H, m), 6.99 (1H, d, ^3J=7.7 Hz), 7.32 (1H, s), 7.38 (1H, br.d, $^3J_{obs}$=6.6 Hz), 7.47 (1H, t, ^3J=7.6 Hz), 9.87 (1H, s), 10.00 (2H, s), NH protons were not assigned.

*Porphyrin **13***. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with porphyrin **9** (0.1 mmol, 96 mg), propane-1,3-diamine (**3**) (0.3 mmol, 22 mg), $Pd(dba)_2$ (2.5 mg, 4 mol %), BINAP (3 mg, 4.5 mol %), absolute dioxane (1 ml) and ^{t}BuONa (0.3 mmol, 29 mg). The reaction mixture was refluxed for 24 hrs, cooled to ambient temperature, diluted with CH_2Cl_2 (5 ml), the residue was filtered off, washed with CH_2Cl_2 (5 ml), combined organic fractions were evaporated *in vacuo*, and chromatographed on silica gel using a gradient of eluents: CH_2Cl_2 – CH_2Cl_2/MeOH 3:1 – CH_2Cl_2/MeOH/NH_3aq 100:20:1–10:14:1. The target compound was eluted with CH_2Cl_2/MeOH/NH_3aq 100:20:3. Yield: 46 mg (49 %), deep-red solid. Mass spectrum (MALDI TOF) *m/z*: 942.7058 $[M]^+$. $C_{62}H_{86}N_8$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: -2.30 (2H, br.s), 1.00 (12H, t, ^3J=7.3 Hz), 1.57 (8H, sextet, ^3J=7.3 Hz), 1.77 (8H, quintet, ^3J=7.3 Hz), 1.88 (4H, quintet, ^3J=6.4 Hz), 2.25 (8H, quintet, $^3J_{obs}$=5.8 Hz), 2.65 (12H, s), 2.93 (4H, t, ^3J=6.4 Hz), 3.37 (4H, t, ^3J=6.4 Hz), 4.03 (8H, t, $^3J_{obs}$=5.8 Hz), 6.92 (4H, d, $^3J_{obs}$=8.1 Hz), 7.80 (4H, d, $^3J_{obs}$=8.1 Hz), 10.26 (2H, s), six NH protons were not assigned. ^{13}C NMR (***???*** MHz, $CDCl_3$, 298 K) δ_C ppm: 14.2 (4C), 14.9 (4C), 22.8 (4C), 26.7 (4C), 32.5 (6C), 33.0 (4C), 40.2 (2C), 42.4 (2C), 96.6 (2C), 111.9 (4C), 118.4 (2C), 131.1 (2C), 133.5 (4C), 136.5 (4C), 141.3 (4C), 142.8 (4C), 145.9 (4C), 148.5 (2C).

*Porphyrin **15***. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with porphyrin **11** (0.05 mmol, 48 mg), trioxadiamine **4** (0.2 mmol, 44 mg), $Pd(dba)_2$ (4.5 mg, 16 mol %), DavePhos (3.5 mg, 18 mol %), absolute dioxane (3 ml) and ^{t}BuONa (0.15 mmol, 15 mg). The reaction mixture was refluxed for 24 hrs, cooled to ambient temperature, diluted with CH_2Cl_2 (5 ml), the residue was filtered off, washed with CH_2Cl_2 (5 ml), combined organic fractions were evaporated *in vacuo*, and chromatographed on silica gel using a gradient of eluents: CH_2Cl_2 – CH_2Cl_2/MeOH 3:1 – CH_2Cl_2/MeOH/NH_3aq 100:20:1–10:14:1. The target compound was eluted with CH_2Cl_2/MeOH/NH_3aq 100:20:2. Yield: 9 mg (15 %), deep-red solid. Mass spectrum (MALDI TOF) *m/z*: 1236.91 $[M]^+$. $C_{76}H_{116}N_8O_6$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: -2.45 (2H, br.s), 0.95 (12H, t, ^3J=7.1 Hz), 1.31 (4H, quintet, ^3J=5.8 Hz), 1.53 (8H, sextet, ^3J=7.2 Hz), 1.72 (8H, quintet, ^3J=7.2 Hz), 1.96 (4H, quintet, ^3J=6.2 Hz), 2.19 (8H, quintet, ^3J=7.2 Hz), 2.66 (12H, s), 2.88 (4H, t, ^3J=6.2 Hz), 3.03 (4H, t, ^3J=6.3 Hz), 3.16 (4H, t, $^3J_{obs}$=4.9 Hz), 3.33 (4H, t, $^3J_{obs}$=4.6 Hz), 3.37 (4H, t, ^3J=6.3 Hz), 3.41–3.67 (12H, m), 3.98 (8H, t, ^3J=7.0 Hz), 7.02 (2H, d, ^3J=7.7 Hz), 7.27 (2H, s), 7.39 (2H, br.d, $^3J_{obs}$=6.7 Hz), 7.50 (2H, br.t, $^3J_{obs}$=6.8 Hz), 10.21 (2H, s), six NH protons were not assigned.

*Porphyrin **19*** was obtained as the second product in the synthesis of porphyrin **15**. Eluent CH_2Cl_2/MeOH 3:1. Yield: 7 mg (12 %), deep-red solid. Mass spectrum (MALDI TOF) *m/z*: 1096.6558 $[M]^+$. $C_{66}H_{93}BrN_6O_3$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: -2.45 (2H, br.s), 0.95 (12H, t, ^3J=7.1 Hz), 1.52 (8H, sextet, ^3J=7.2 Hz), 1.68–1.75 (10H, m), 1.90 (2H, quintet, ^3J=6.7 Hz), 2.18 (8H, quintet, ^3J=6.9 Hz), 2.64 (12H, s), 2.87 (2H, br.s), 2.94 (2H, br.s), 3.14 (2H, br.s), 3.28 (2H, t, ^3J=6.2 Hz), 3.37 (2H, br.s), 3.56 (6H, br.s), 3.96 (8H, br.s), 7.04 (1H, d, ^3J=7.8 Hz), 7.28 (1H, s), 7.41 (1H, d, ^3J=7.1 Hz), 7.48 (1H, t, ^3J=7.6 Hz), 7.60 (1H, t, ^3J=7.5 Hz), 7.93 (1H, d, ^3J=8.2 Hz), 8.01 (1H, d, ^3J=8.1 Hz), 8.27 (1H, s), 10.22 (2H, s), three NH protons were not assigned.

*Porphyrin **16***. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with porphyrin **11** (0.05 mmol, 48 mg), dioxadiamine **12** (0.2 mmol, 41 mg), $Pd(dba)_2$ (4.5 mg, 16 mol %), DavePhos (3.5 mg, 18 mol %), absolute dioxane (3 ml) and ^{t}BuONa (0.15 mmol, 15 mg). The reaction mixture was refluxed for 24 hrs, cooled to ambient temperature, diluted with CH_2Cl_2 (5 ml), the residue was filtered off, washed with CH_2Cl_2 (5 ml), combined organic fractions were evaporated *in vacuo*, and chromatographed on silica gel using a gradient of eluents: CH_2Cl_2 – CH_2Cl_2/MeOH 3:1 – CH_2Cl_2/MeOH/NH_3aq 100:20:1–10:14:1. The target compound was eluted with CH_2Cl_2/MeOH/NH_3aq 100:20:2. Yield: 18 mg (30 %), deep-red solid. Mass spectrum (MALDI TOF) *m/z*: 1204.9049 $[M]^+$. $C_{76}H_{116}N_8O_4$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: -2.43 (2H, br.s), 0.97 (12H, t, ^3J=7.0 Hz), 1.43 (4H, quintet, ^3J=6.6 Hz), 1.49–1.57 (12H, m), 1.69–1.76 (12H, m), 1.95 (4H, quintet, ^3J=5.9 Hz), 2.21 (8H, br.quintet, $^3J_{obs}$=6.2 Hz), 2.53 (4H, t, ^3J=7.0 Hz), 2.68 (12H, s), 3.14 (4H, br.t, $^3J_{obs}$=5.1 Hz), 3.25–3.45 (12H, m), 3.57 (4H, br.t, $^3J_{obs}$=4.6 Hz), 4.00 (8H, t, ^3J=7.0 Hz), 7.02 (2H, d, ^3J=7.1 Hz), 7.30 (2H, s), 7.43 (2H, br.d, $^3J_{obs}$=5.6 Hz), 7.51 (2H, t, ^3J=7.3 Hz), six NH protons were not assigned. ^{13}C NMR ($CDCl_3$, 298 K) δ_C ppm: 14.2 (4C), 14.4 (4C), 22.8 (4C), 26.3 (2C), 26.4 (2C), 26.7 (4C), 29.5 (2C), 32.5 (6C), 33.0 (4C), 39.4 (2C), 42.3 (2C), 68.7 (2C), 69.4 (2C), 70.5 (2C), 70.8 (2C), 96.6 (2C), 112.7 (2C), 118.1 (2C), 118.6 (2C), 122.8 (2C), 128.2 (2C), 136.4 (4C), 141.2 (4C), 143.0 (4C), 145.0 (4C), 148.0 (2C), 2 quaternary carbon atoms were not assigned.

*Porphyrin **20*** was obtained as the second product in the synthesis of porphyrin **16**. Eluent CH_2Cl_2/MeOH 10:1–3:1. Yield: 10 mg (18 %), deep-red solid. Mass spectrum (MALDI TOF) *m/z*: 1080.6632 $[M]^+$. $C_{66}H_{93}BrN_6O_2$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: -2.35 (2H, br.s), 0.95 (12H, br.t, $^3J_{obs}$=6.2 Hz), 1.25–1.63 (20H, br.m), 1.72 (8H, br.s), 1.90 (4H, br.s), 2.20 (8H, br.t, $^3J_{obs}$=7.0 Hz), 2.65 (12H, s), 2.94–3.65 (24H, br.m), 3.97 (8H, br.s), 7.01 (1H, br.d, $^3J_{obs}$=7.0 Hz), 7.27 (1H, s), 7.40 (1H, br.d, $^3J_{obs}$=6.1 Hz), 7.50 (1H, br.t, $^3J_{obs}$=7.0 Hz), 7.60 (1H, br.y, $^3J_{obs}$=7.2 Hz), 7.95 (1H, d, ^3J=7.5 Hz), 8.03 (1H, d, ^3J=8.2 Hz), 8.28 (1H, 2), 10.23 (2H, s), six NH protons were not assigned.

*Conjugate **28***. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with Zn porphyrinate **27** (0.15 mmol, 113 mg), azacrown derivative **25** (0.15 mmol, 64 mg), $Pd(dba)_2$ (7 mg, 8 mol %), BINAP (8.5 mg, 9 mol %), absolute dioxane (2 ml) and ^{t}BuONa (0.23 mmol, 22 mg). The reaction mixture was refluxed for 24 hrs, cooled to ambient temperature, diluted with CH_2Cl_2 (5 ml), the residue was filtered off, washed with CH_2Cl_2 (5 ml), combined organic fractions were evaporated *in vacuo*, dissolved in CH_2Cl_2, washed with water (5 ml) and dried over molecular sieves. Solvent was again evaporated *in vacuo* and the residue was chromatographed on silica gel using a gradient of eluents: CH_2Cl_2 – CH_2Cl_2/MeOH 3:1. The target compound was eluted with CH_2Cl_2/MeOH 10:1. Yield: 24 mg (15 %), deep-red solid. UV-Vis (CH_3CN) λ nm (lgε): 409 (5.55), 539 (4.32), 574 (4.13). Mass spectrum (MALDI TOF) *m/z*: 1095.5976 $[M]^+$. $C_{64}H_{85}N_7O_5Zn$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 0.97 (6H, t, *J*=7.3 Hz), 1.51 (4H, sextet, *J*=7.3 Hz), 1.69 (4H, quintet, *J*=7.4 Hz), 2.12 (4H, quintet, *J*=7.4 Hz), 2.25 (2H, br.s), 2.51 (6H, s), 2.70–3.50 (26H, br.m), 3.11 (2H, br.s), 3.34 (2H, t, *J*=6.2 Hz), 3.41 (6H, s), 3.43 (6H, s), 3.71 (4H, t, *J*=7.4 Hz), 6.06 (1H, br.s), 6.27 (2H, br.s), 6.80 (1H, t, J_{obs}=6.9 Hz), 6.92 (1H, d, J_{obs}=6.8 Hz), 7.14 (1H, s), 7.32 (1H, d, J_{obs}=6.2 Hz), 7.44 (1H, t, *J*=7.6 Hz), 9.42 (1H, s), 9.82 (2H, s), two NH protons were not assigned. ^{13}C NMR ($CDCl_3$, 298 K) δ_C ppm: 11.5 (2C), 12.1 (2C), 14.1 (2C), 15.1 (2C), 22.7 (2C), 26.3 (2C), 28.5 (1C), 32.4 (2C), 33.0 (2C), 41.6 (1C), 41.7 (1C), 51.9 (2C), 57.3 (1C), 68.8 (2C), 69.4 (4C), 69.6 (4C), 95.8 (1C), 96.7 (2C), 102.6 (1C), 112.5 (1C), 118.8 (1C), 123.0 (2C), 128.0 (1C), 135.6 (2C), 137.8 (2C), 138.4 (2C), 140.9 (2C), 144.4 (1C), 146.8 (2C), 146.9 (2C), 147.5 (2C), 147.7 (2C), 149.1 (1C), 149.2 (1C), four quaternary carbon atoms were not assigned.

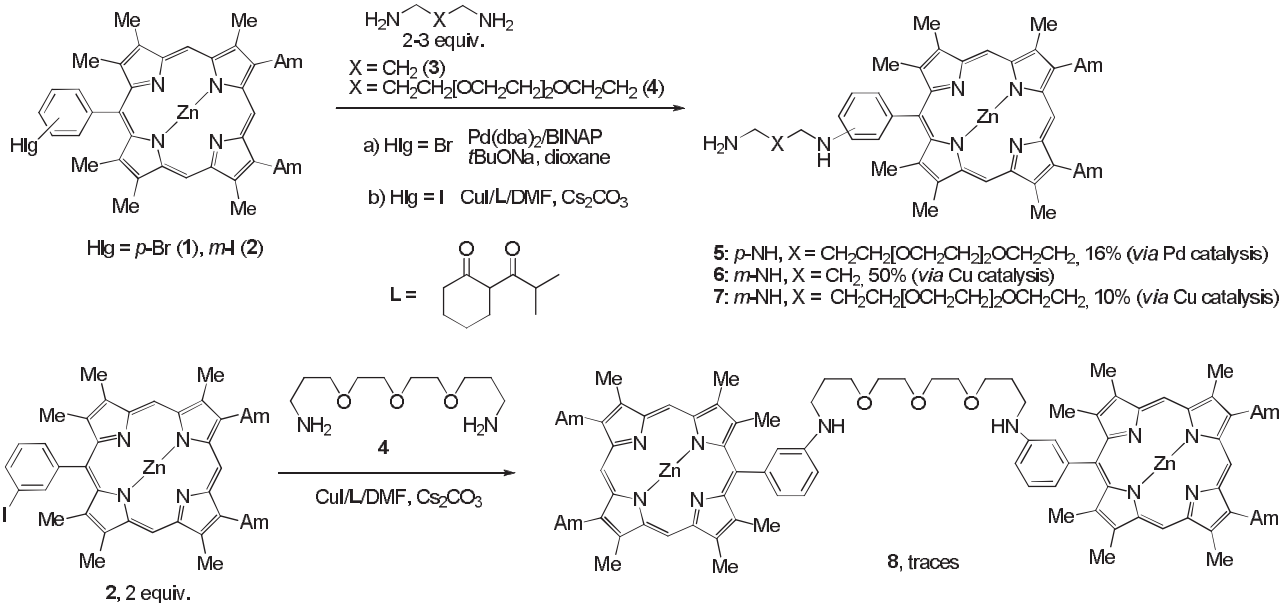
*Conjugate **29***. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with Zn porphyrinate **10** (0.11 mmol, 111 mg), azacrown derivative **25** (0.22 mmol, 94 mg), $Pd(dba)_2$ (5 mg, 8 mol %), BINAP (6 mg, 9 mol %), absolute dioxane (2 ml) and ^{t}BuONa (0.33 mmol, 32 mg). The reaction mixture was refluxed for 24 hrs and then

worked up in a similar manner as described for compound **28**. The target compound was eluted with CH_2Cl_2/MeOH/NH_3aq 100:35:6–10:4:1. Yield: 28 mg (15 %), deep-red solid. UV-Vis (CH_3CN) λ nm (lgε): 417 (4.80), 546 (3.45), 578 (3.17). Mass spectrum (MALDI TOF) *m/z*: 1707.03 $[M]^+$. $C_{100}H_{142}N_{10}O_{10}Zn$. ^1H NMR ($CDCl_3$, 298 K) δ_H ppm: 0.96 (12H, t, *J*=7.3 Hz), 1.53 (8H, sextet, *J*=7.0 Hz), 1.73 (8H, quintet, *J*=6.8 Hz), 2.01 (4H, br.s), 2.18 (8H, quintet, *J*=6.4 Hz), 2.56 (12H, s), 2.70 (8H, br.s), 3.21 (4H, br.s), 3.35–3.68 (48H, m), 3.94 (8H, t, *J*=7.1 Hz), 6.44 (2H, d, J_{obs}=5.4 Hz), 6.63 (4H, d, J_{obs}=7.0 Hz), 6.93 (4H, d, J_{obs}=7.8 Hz), 7.10 (2H, t, *J*=7.8 Hz), 7.77 (4H, d, J_{obs}=7.8 Hz), 10.10 (2H, s), four NH protons were not assigned. 14.2 (4C), 15.5 (4C), 22.8 (4C), 26.7 (4C), 29.6 (2C), 32.5 (4C), 33.1 (4C), 42.0 (2C), 42.2 (2C), 53.6 (4C), 59.3 (2C), 69.7–70.6 (m, 20C), 97.0 (2C), 111.7 (2C), 112.0 (4C), 114.3 (2C), 118.4 (2C), 128.7 (2C), 129.0 (4C), 133.7 (4C), 138.2 (4C), 142.8 (4C), 146.2 (4C), 148.2 (2C), 148.4 (4C), four quaternary carbon atoms were not assigned.

*Conjugate **30***. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with porphyrin **9** (0.1 mmol, 96 mg), azacrown derivative **26** (0.2 mmol, 76 mg), $Pd(dba)_2$ (9 mg, 16 mol %), BINAP (11 mg, 18 mol %), absolute dioxane (1 ml) and ^{t}BuONa (0.3 mmol, 29 mg). The reaction mixture was refluxed for 24 hrs and then worked up in a similar manner as described for compound **28**. The target compound was eluted with CH_2Cl_2/MeOH/NH_3aq 100:20:3. Yield: 32 mg (20 %), deep-red solid. Mass spectrum (MALDI TOF) *m/z*: 1557.04 $[M]^+$. $C_{96}H_{136}N_{10}O_8$. ^1H NMR ($CDCl_3$, 298 K) δ_H ppm: -2.40 (2H, br.s), 0.95 (12H, t, *J*=7.2 Hz), 1.51 (8H, sextet, *J*=7.3 Hz), 1.71 (8H, quintet, *J*=7.4 Hz), 2.15 (4H, quintet, *J*=5.8 Hz), 2.19 (8H, quintet, *J*=7.1 Hz), 2.61 (12H, s), 2.84 (8H, br.s), 3.42 (4H, t, *J*=6.3 Hz), 3.53 (4H, t, *J*=6.1 Hz), 3.64 (36H, br.s), 3.98 (8H, t, *J*=7.0 Hz), 6.60 (2H, d, *J*=7.6 Hz), 6.69 (2H, d, J_{obs}=7.1 Hz), 6.86 (2H, br.s), 6.98 (4H, d, J_{obs}=8.1 Hz), 7.17 (2H, t, *J*=7.7 Hz), 7.79 (4H, d, J_{obs}=8.1 Hz), 10.20 (2H, s), four NH protons were not assigned. ^{13}C NMR ($CDCl_3$, 298 K) δ_C ppm: 14.2 (4C), 14.9 (4C), 22.8 (4C), 26.7 (4C), 29.5 (2C), 32.5 (4C), 33.0 (4C), 42.2 (2C), 42.4 (2C), 54.4 (4C), 60.7 (2C), 69.9 (4C), 70.2 (4C), 70.5 (4C), 70.9 (4C), 96.6 (2C), 111.1 (2C), 112.0 (4C), 113.7 (2C), 118.1 (4C), 122.5 (2C), 129.1 (2C), 133.5 (4C), 136.5 (4C), 141.3 (4C), 142.8 (4C), 145.8 (2C), 148.3 (2C), 148.4 (2C), four quaternary carbon atoms were not assigned.

Results and Discussion

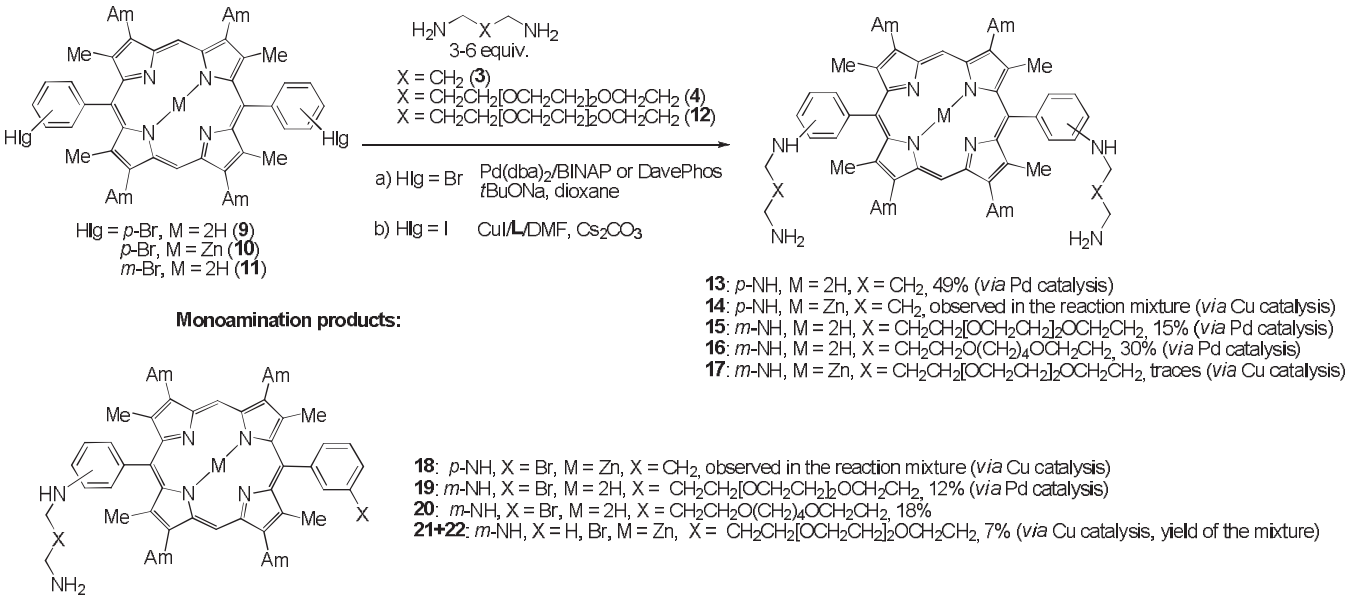
In the course of our investigation we proposed several approaches to create a combination of the porphyrin moiety with azacrown ethers. The first route employed the diamine or oxadiamine linker between these two macrocycles, and for this purpose first the amination reactions of *meso*-(halogenophenyl)porphyrins **1** and **2** with propane-1,3-diamine (**3**) and trioxadiamine **4** were studied. Amination of *meso*(4-bromophenyl)porphyrin **1** taken as its Zn complex was conducted using a standard Pd-catalyzed procedure in the presence of $Pd(dba)_2$/BINAP system (dba=dibenzylideneacetone, BINAP=2,2'-bis(diphenylphosphino)-1,1'-binaphthalene). The reaction was carried out using 3 equiv. of the trioxadiamine **4** in boiling dioxane with ^{t}BuONa as a base and provided 16 % yield of the target derivative **5** (Scheme 1). It should be noted that the same reaction with free porphyrin was unsuccessful and did not provide the desired coupling product. It is of undoubtful interest that the Cu^I-catalyzed amination of 3-iodophenyl substituted Zn porphyrinate **2** with excess of propane-1,3-diamine (**3**) was substantially more successful as it provided *ca* 50 % yield of the amination product **6**. 2-(*iso*-Butyryl)cyclohexanone ligand (**L**) was used in the reaction run in DMF at 110 °C. The amination of the same prophyrinate **2** with trioxadiamine **4** carried out under similar conditions was less efficient and compound **7** was isolated in 10 % yield (Scheme 1). Having obtained such encouraging results, we have explored the possibility to synthesize a bisporphyrin compound with trioxadiamine linker between two porphyrin moieties and reacted 2 equiv. of **2** with trioxadiamine **4** under the catalysis by CuI/**L**/DMF at 140 °C. However, in this case we have managed to isolate the target compound **8** in trace amounts and it could not be purified from various admixtures. It was detected by MALDI-TOF mass spectrometry (*m/z*=1560.60 $[M]^+$). This result demonstrates, as enough general rule, that *N,N'*-diarylation of diamines and oxadiamines is often



Scheme 1.

problematic under Cu^{I} catalysis,[34,35] what is unlikely for Pd^{0}-catalyzed diarylation.[36,37]

Contrary to the amination of 4-bromophenylporphyrin (**1**), the Pd^{0}-catalyzed reaction of the free di-*meso*-(4-bromophenyl)porphyrin (**9**) with excess of propane-1,3-diamine was quite successful and provided 49 % yield of the diamination product **13** (Scheme 2). The attempt to use Cu^{I} catalysis by reacting zinc di-*meso*-(4-bromophenyl)porphyrinate **10** with the same amine was unsuccessful as it has given the target diamination product **14** and the product of monoamination **18** only in small amounts in the reaction mixture and they could not be separated from the starting porphyrin **10** by the column chromatography. Compounds **14** and **18** were detected by MALDI-TOF spectra (*m/z*=1005.64 and 1011.44 $[M+H]^{+}$, resp.). Free porphyrin **11** with 3-bromophenyl substituent have reacted with excess of trioxadiamine **4** under Pd^{0} catalysis conditions and have given the corresponding diamination product **15** in 15 % after column chromatography. Also the monoamination product **19** was isolated in 12 % yield. A similar reaction with dioxadiamine **12** provided bis(diamino) derivative **16** in a better 30 % yield due to easier chromatographic isolation of a less polar compound. The yield of the product of monoamination **20** was 18 %. These reactions were conducted in the presence of another ligand DavePhos (2-dimethylamino-2'-dicyclohexylphosphino)biphenyl which promotes diamination of dihalogenoaryl derivatives (*m*-bromophenyl porphyrin derivative is less active in the catalytic amination than *p*-bromophenyl derivative). The reaction of Zn porphyrinate **12** with two 4-bromophenyl substituents in the porphyrin core catalyzed



Scheme 2.

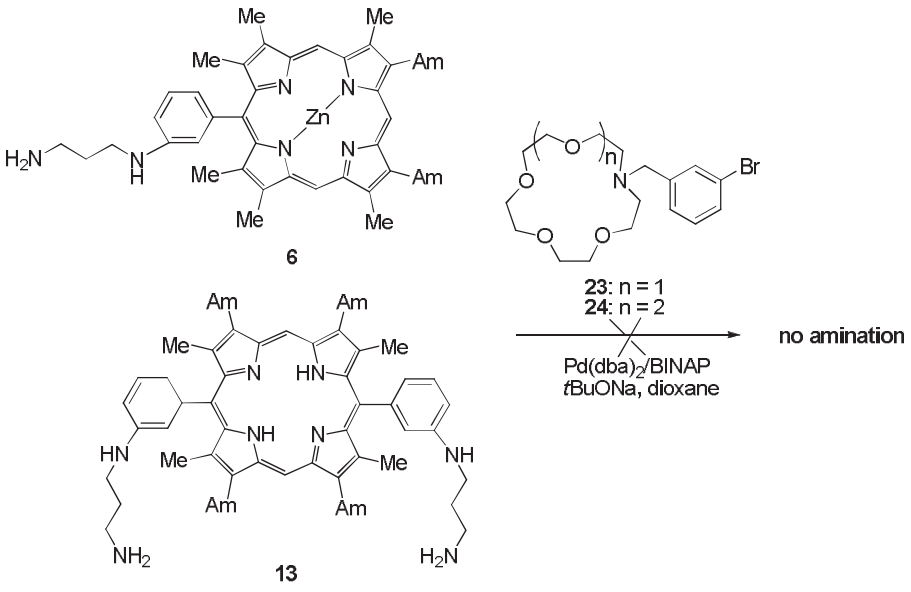
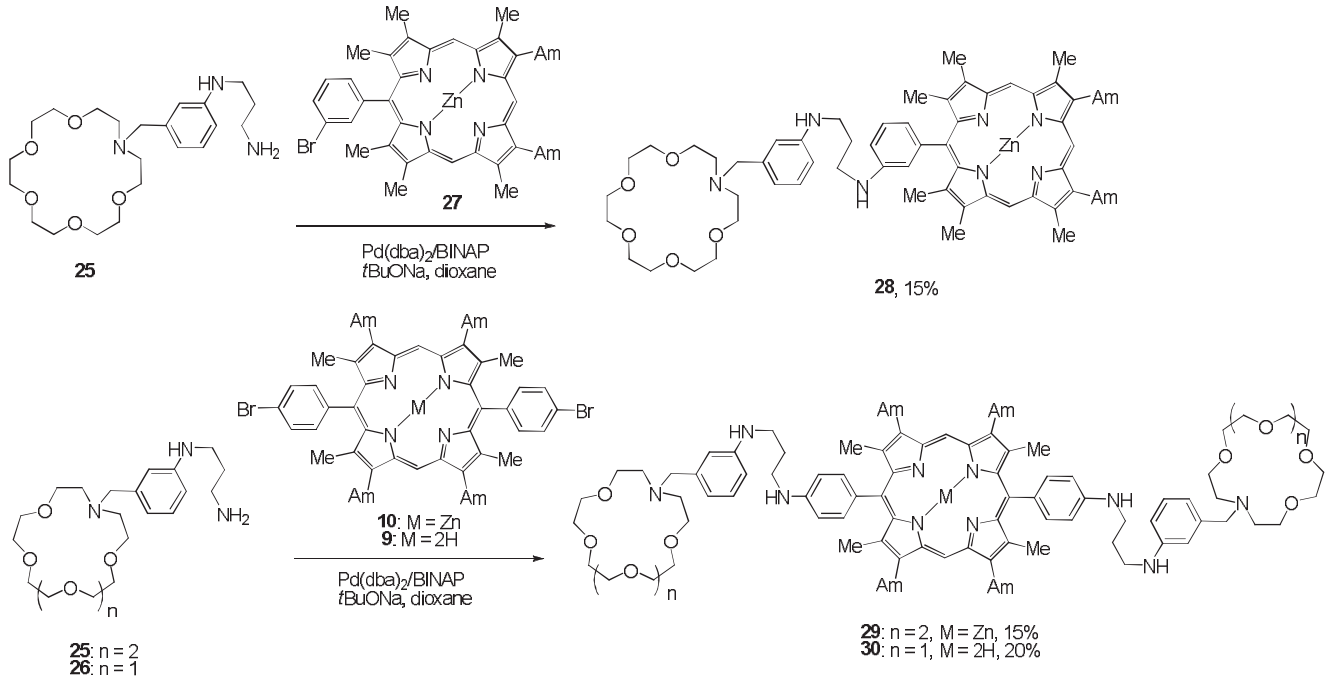


Figure 1. Unsuccessful attempts of porphyrin – azacrown ethers conjugation.



Scheme 3.

by CuI/**L**/DMF was inefficient and led to the products of monoamination **21** and **22** (in the latter compound the resting C-Br bond was reduced) obtained as an inseparable mixture in *ca* 7 % yield (*m/z*=1078.49 and 1156.39 $[M]^+$, resp.), while the target diamination product **18** was isolated in trace amounts and detected using MALDI-TOF mass-spectrometry (*m/z*=1296.79 $[M]^+$).

In order to obtain conjugates of azacrown ethers with porphyrins we first tried the Pd^0-catalyzed coupling of mono- and diaminosubstituted porphyrins **6** and **13** with *N*-(3-bromobenzyl) substituted azacrown ethers **23** and **24** (Figure 1). However, in all attempts we did not observe the formation of the amination products even in the reaction mixtures and noted the reduction of the C-Br bond in azacrown derivatives. Thus this way of constructing conjugates was abandoned.

Another approach for constructing azacrown-porphyrin conjugates was more successful (Scheme 3). At first amino derivatives of *N*-benzyl substituted crown ethers **25** and **26** were synthesized by the Pd^0-catalyzed amination of 3-bromobenzyl substituted precursors according to a previously described procedure.[33] Then compounds **25** and **26** were introduced in the second catalytic amination reactions with Zn 3-bromophenylporphyrinate **27** and with di-*meso*-(4-bromophenyl)porphyrins **9** and **10** (free base and Zn complex, resp.). All reactions were enough successful and provided bismacrocycle **28** or trismacrocycles **29**, **30** in comparable 15–20 % yields (Scheme 3). Again it was shown that monophenyl substituted porphyrin could react normally only as its Zn complex **1** while diphenyl derivative provided similar yields of the diamination products both as free base **9** and in the form of the Zn complex **10**.

Compounds **28–30** can be viewed as di- or tritopic ligands interesting for the synthesis of heterodi- or heterotrinuclear complexes. In these polymacrocycles the trimethylene diamine linker between porphyrin and azacrown moieties could have been replaced for a longer trioxadiamine fragment which contains several donor atoms. This could have led to the synthesis of pentatopic ligands, unfortunately, all our attempts to change trimethylenediamine linker for trioxadiamine failed. Trioxadiamine derivatives of either *meso*-phenylporphyrin or *N*-benzyl azacrown ether would not participate in the Pd^0-catalyzed coupling reactions similar to those shown in Figure 1 and Scheme 3. They led only to partial reduction of C-Br bonds and formation of complex mixtures of unidentified compounds indicating severe limitations of the process.

The UV-Vis spectrum of conjugate **28** contains a strong Soret band (λ=409 nm, lgε=5.55) and two less intensive Q bands (λ=539 and 574 nm, lgε=4.32 and 4.13, respectively). The comparison with the starting zinc porphyrinate **1** shows insignificant bathochromic shifts of all bands by 2–3 nm and a notable increase of the intensity of Q bands. The fluorescence spectrum of compound **28** possesses two bands of almost equal intensities at 589 and 641 nm. The UV-Vis spectrum of conjugate **29** contains a strong Soret band (λ=417 nm, lgε=4.80) and two less intensive Q bands (λ=546 and 578 nm, lgε=3.45 and 3.17, respectively). The comparison with the starting zinc porphyrinate **10** shows small bathochromic shifts of all bands by 3–6 nm and a small increase of the intensity of the Soret band and one Q band. The fluorescence spectrum of compound **29** possesses two bands at 594 and 648 nm, the first being more intensive. It is worthnoting that the absorption of monophenyl substituted porphyrin **28** in the visible range is substantially stronger than that of di-*meso*-phenyl substituted porphyrin **29**.

We have investigated the dependence of the spectral properties of the compounds **28** and **29** possessing one and two 1-aza-18-crown-6 moieties in their structures on the presence of seventeen metal cations in order to find perspective

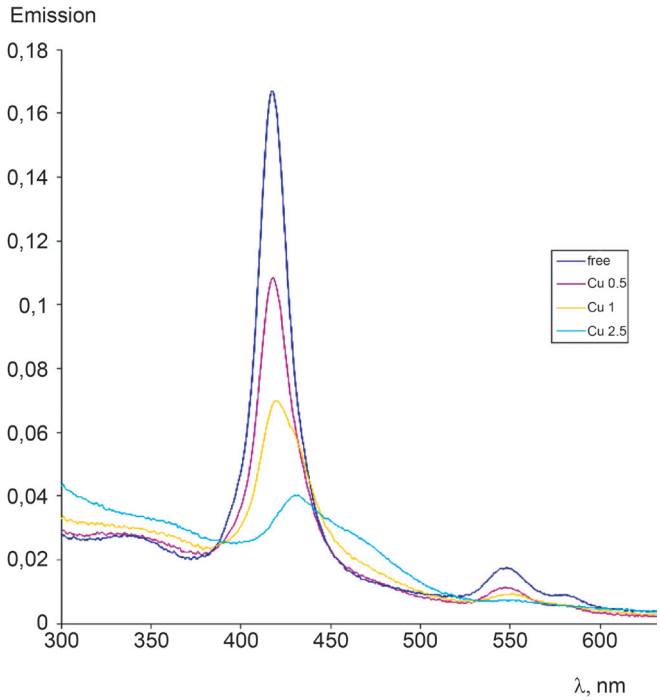


Figure 2. Evolution of UV-vis spectrum of trismacrocycle **29** after addition of 0.5, 1 and 2.5 equiv. $Cu(ClO_4)_2$ (MeCN, C=3.33·10^{-6} M).

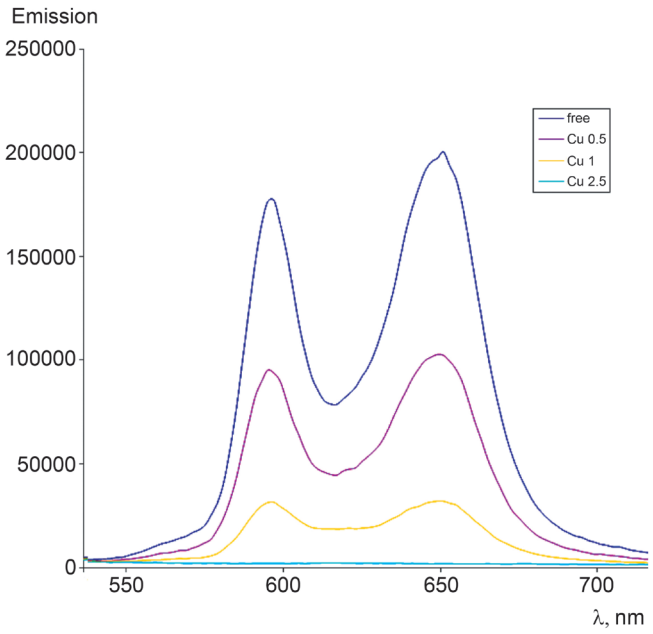


Figure 3. Evolution of the fluorescence of trismacrocycle **29** after addition of 0.5, 1 and 2.5 equiv. $Cu(ClO_4)_2$ (MeCN, C=3.33·10^{-6} M, λ_{ex}=418 nm).

optical chemosensors. For this purpose we have measured UV-Vis and fluorescent spectra of these polymacrocycles in MeCN adding 0.5, 1 and 2.5 equiv. of corresponding metal perchlorates. Excitation of bismacrocycle **28** was carried out at 410 nm, that of trismacrocycle **29** – at 418 nm. As for bismacrocycle **28**, no significant changes in its electronic and fluorescent spectra could be noted for the majority of metals except for Cu^{II} which led to a partial decrease of the intensity of the absorption peak at 409 nm (Figure 1S) and produced two-fold quenching of the emission intensity (Figure 2S). Pb^{II} has also caused notable quenching of fluorescence, other metals have changed it insignificantly. The maxima of absorption and emission bands did not change in all cases studied. We have investigated the dependence of the electronic and fluorescent spectra of bismacrocycle **28** on the amount of copper perchlorate added. In the UV-Vis spectra one can observe gradual weakening of the absorption maximum at 409 nm up to 10 equiv. of Cu^{II} added, its further attenuation together with bathochromic shift to 425 nm occurred in the presence of 20–30 equiv. of Cu^{II} salt (Figure 3S). Fluorescence was quenched gradually without any shift of two maxima at 589 and 641 nm, and with 30 equiv. of $Cu(ClO_4)_2$ it was almost fully quenched (Figure 4S).

The addition of 2.5 equiv. of different metal perchlorates to the solution of trismacrocycle **29** did not result in significant changes in its absorption and emission spectra (Figures 5S and 6S), except for $Cu(ClO_4)_2$ which dramatically decreased the intensity of absorption and led to a bathochromic shift of its maximum (from 417 to 432 nm, Figure 3S). The quenching of emission with Cu^{II} was almost total (Figure 6S) while Pb^{II} has decreased it only by 25 %, and the ligand was quite insensitive for other metal cations. It is interesting that the addition of 0.5 and 1 equiv. of Cu^{II} gradually decreased the absorption (Figure 2), however, it did not result in the shift of the absorption maximum both of Soret and Q bands. The addition of the second equivalent has given rise to above mentioned bathochromic shift of the Soret band and simultaneously the Q band almost totally disappeared. Also, upon the addition of 0.5 and 1 equiv. of Cu^{II} emission gradually decreased (*ca* 2 and 6 times, resp.), but with the second equivalent it was fully quenched (Figure 3). These facts might be explained by the formation of a non-emissive dicopper complex with trismacrocycle **29** possessing two azacrown fragments each capable of complexing with one Cu^{II} cation.

Special experiments have been undertaken to verify cross-selectivity of the ligand **29** towards Cu^{II} using Na^{I}, K^{I}, Mg^{II}, Ca^{II}, Ba^{II}, Zn^{II}, Pb^{II} and Hg^{II} perchlorates which can be viewed as the most expected interfering ions. The UV-Vis and fluorescence spectra in all cases were absolutely the same as in the presence of sole copper perchlorate (weak maximum at 432 nm and no emission). We have evaluated the detection limits of Cu^{II} ions by the ligand **29** and found out that it was 1.2 mM by UV spectrophotometer and 0.23 mM by spectrofluorimeter. These figures are among the best judging by the analysis of the literature data. Indeed, there are several recently developed fluorimetric chemosensors for copper which provided detection at 1–10 mM level,[38-42] while there is only one sensor based on thiacalix[4]crown ether with two pyrene fluorophores able to detect 40 nm concentration of Cu^{II}.[43] It should be also noted that there is a plenty of colorimetric detectors of copper ions,[44-51] however, their detection limits are not as low, moreover, some of them are indeed not chemosensors but rather molecular probes as they sense also other cations like Hg^{II} or Fe^{III}. Thus conjugate **29** can be proposed as a perspective two-channel fluorimetric and colorimetric chemosensor for Cu^{II} ions.

Conclusions

To sum up, we have showed the possibility to decorate porphyrins with diamine and oxadiamine podands *via* Pd^0 and Cu^I-catalyzed amination reactions, however, the palladium catalysis proved to be more universal. Pd^0-catalyzed amination was applied to the synthesis of bis- and trismacrocyclic conjugates of porphyrin with azacrown ethers using trimethylenediamine linkers. This target can be achieved using only one approach, *i.e.* combining *meso*-(bromophenyl) substituted porphyrins with aminobenzyl derivatives of azacrown ethers. All these compounds can be used as polytopic ligands in the synthesis of polynuclear metal complexes. The properties of two compounds, bismacrocycle **28** and trismacrocycle **29**, to perform as colorimetric and fluorescent sensors for metal cations were investigated, and ligand **29** possessing two 1-aza-18-crown-6 moieties arranged symmetrically around the porphyrin core was found to be enough selective for Cu^{II} in the presence of other metals by strong emission quenching caused by copper ions.

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