

Porphyrin-Containing Polymacrocycles: Synthesis and Evaluation as Fluorescent Detectors of Metal Cations

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Using Pd(0)-catalyzed amination reaction of zinc 5,15-bis(4-bromophenyl)porphyrinate with diazatrioxamacrocycle – derivative of 3,3'-disubstituted biphenyl – a series of polymacrocyclic compounds was obtained. The investigation of their fluorescence in the presence of 18 metal cations revealed that two of them can act as molecular probes for Cu(II), Al(III) and Cr(III) by the fluorescence quenching. Tri- and tetramacrocyclic compounds of another structure were synthesized by the Pd(0)-catalyzed arylation of cryptands comprising central diazacrown ether moieties using zinc 5-(4-bromophenyl)porphyrinate. One of these compounds was characterized as a fluorescent chemosensor for Cu(II).

Keywords: Porphyrins, diazacrown ethers, polymacrocycles, Pd catalysis, amination, fluorescence, detection.

Порфирин-содержащие полимакроциклы: синтез и оценка в качестве флуоресцентных детекторов катионов металлов

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С использованием Pd(0)-катализируемой реакции аминирования цинкового комплекса 5,15-бис(4-бромфенил)порфирина с диазатриоксамacroциклом – производным 3,3'-дизамещенного бифенила – получена серия полимакроциклических соединений. Исследование их флуоресценции в присутствии катионов 18 металлов показало, что два из них могут выступать в качестве молекулярных проб на катионы Cu(II), Al(III) и Cr(III) за счет тушения флуоресценции. Три- и тетрамакроциклические соединения другого строения синтезированы Pd(0)-катализируемым аминированием криптанов, содержащих центральный фрагмент диазакраун-эфира с использованием цинкового комплекса 5-(4-бромфенил)порфирина. Одно из этих соединений охарактеризовано как флуоресцентный хемосенсор на катионы Cu(II).

Ключевые слова: Порфирины, диазакраун-эфиры, полимакроциклы, Pd катализ, аминирование, флуоресценция, детектирование.

Introduction

Catalytic approaches to polymacrocyclic compounds based on porphyrins are well documented. The vast majority of such molecules are porphyrin dyads, triads and parent compounds, while the conjugates with other nitrogen-containing macrocycles are still enough rare. The synthesis of directly *meso-meso*-linked porphyrins without any spacer can be achieved *via* Ni(II)-catalyzed oxidative coupling of *meso*-bromoporphyrins^[1] or using Suzuki coupling.^[2,3] The chemistry of porphyrin oligomers built using various aromatic, heteroaromatic or other unsaturated linkers is much more explored as they can bring additional structural and physicochemical properties to a molecule. For this purpose Suzuki,^[4–6] Stille,^[7,8] Heck,^[9] and Sonogashira^[10,11] couplings were successfully applied. Triazolyl linker can be easily introduced in the porphyrin dyads and triads by epy so-called click reactions,^[12–14] and the application of Buchwald-Hartwig amination reactions was reported for the synthesis of *bis*porphyrin compounds in which two macroheterocycles were linked with a simple NH fragment,^[15] a series of di- an polyporphyrin compounds was obtained by a similar approach in which diamines or diazacrown ether moieties served as linkers.^[16,17] While porphyrins possess extremely interesting photophysical properties together with their unique binding of metal cations, they have not yet become a widespread platform for creating colorimetric or fluorimetric chemosensors. The examples are still scarce, to mention the porphyrin-terpyridine conjugate which can detect Cd(II) with moderate selectivity,^[18] *tetrakis*(4-methoxyphenyl)porphyrin for sensing Ag(I),^[19] and another detector of the same cation employing the combination of the porphyrin and quinoline moieties.^[20] Recently we have described the catalytic synthesis of porphyrin conjugates with azacrown ethers and tested them as fluorimetric detectors of metal cations.^[21,22] In continuation of this research here we report the synthesis of the polymacrocyclic derivatives of porphyrin comprising biphenyl-based diazatrioxa-macrocycle and cryptands with diazacrown ether moieties.

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. UV-Vis spectra were recorded with Agilent Cary 60 spectrophotometer in MeCN, spectra of fluorescence were obtained with Hitachi 2700 spectrofluorometer in acetonitrile (UHPLC grade). *Rac*-BINAP and DavePhos ligands, sodium *tert*-butoxide, were purchased from Sigma-Aldrich Co and used without further purification, Pd(dba)₂ was synthesized according to the method described.^[23] Macrobicycle **3** was obtained according to the described method,^[24] macrobicycles **12–14** were synthesized according to a published procedure,^[25] zinc porphyrinates **4**, **15** and **18** were obtained by method described in ref.^[26] Column chromatography was carried out using silica gel 40–63 nm (Fluka). Acetonitrile of UHPLC grade was used without additional purification, dioxane was successively distilled over NaOH and sodium. Dichloromethane was distilled over CaH₂, methanol was used freshly distilled.

Method for the synthesis of polymacrocycles 5–8, 16, 17, 19, 20. A two-neck flask equipped with a magnetic stirrer and reflux

condenser, flushed with dry argon, was charged with corresponding amounts of Pd(dba)₂, DavePhos, zinc porphyrinates **4** or **18**, macrocyclic compound **3** or cryptands **12–14**, absolute dioxane and sodium *tert*-butoxide. The reaction mixture was stirred under reflux for 24h, cooled down to ambient temperature, the residue was filtered off, washed with CH₂Cl₂ (5 ml), the combined organic fractions were evaporated *in vacuo* and the residue was chromatographed on silica gel using a sequence of eluents: CH₂Cl₂, CH₂Cl₂ – MeOH 500:1 – 3:1.

Trismacrocyclic compound 5. Obtained from zinc porphyrinate **4** (0.1 mmol, 102 mg), macrocycle **3** (0.2 mmol, 74 mg) in the presence of Pd(dba)₂ (16 mol %, 9 mg), DavePhos (18 mol %, 7 mg), *t*BuONa (0.3 mmol, 29 mg) in 2 ml dioxane. Eluent: CH₂Cl₂–MeOH 100:1. Yield 14 mg (9 %), dark-red crystalline powder. M.p. 195–200 °C. *m/z* (MALDI-TOF) found: 1596.9069. C₁₀₀H₁₂₄N₈O₆Zn requires 1596.8935 [M]⁺. UV-Vis (CH₃CN) λ_{max} (lgε) nm: 416 (5.29). ¹H NMR (CDCl₃, 298 K) δ_H ppm: 1.00 t (12H, ³J=7.3 Hz), 1.54–1.61 m (12H), 1.78 quintet (8H, ³J=7.4 Hz), 2.17–2.26 m (12H), 2.63 s (12H), 3.24 br.t (4H, ³J_{obs}=4.7 Hz), 3.31 br.s (4H), 3.33–3.63 m (16H), 3.67 br.t (4H, ³J_{obs}=4.9 Hz), 4.00 br.s (8H), 4.21 t (4H, ³J=6.1 Hz), 5.70 br.s (2H), 6.12 br.s (2H), 6.90 d (2H, ³J=7.2 Hz), 7.00 t (2H, ³J=7.1 Hz), 7.16 d (2H, ³J=7.3 Hz), 7.28 d (2H, ³J=8.5 Hz), 7.36–7.43 m (8H), 7.87 d (4H, ³J=7.6 Hz), 10.14 s (2H) (NH protons were not assigned). ¹³C NMR (CDCl₃, 298 K) δ_C ppm: 14.2 (4C), 15.4 (4C), 22.9 (4C), 26.9 (4C), 27.8 (2C), 27.9 (2C), 32.7 (4C), 33.2 (4C), 42.9 (2C), 49.1 (2C), 68.5 (2C), 70.5 (2C), 70.7 (2C), 70.8 (2C), 70.9 (2C), 80.0 (2C), 97.2 (2C), 111.2 (2C), 113.1 (2C), 116.9 (2C), 118.9 (2C), 120.2 (4C), 120.4 (2C), 129.0, 129.1, 134.1 (4C), 137.2, 137.9, 141.9, 143.1, 146.3, 147.2, 147.5, 148.1, 149.3 (6 quaternary carbon atoms of the biphenyl moieties were not assigned, carbon atoms of the porphyrin moiety were not integrated).

Bismacrocyclic 6 was isolated as the second compound in the synthesis of *trismacrocyclic 5*. Eluent: CH₂Cl₂–MeOH 500:1. Yield 20 mg (16 %), dark-red crystalline powder. M.p. 148–150 °C. *m/z* (MALDI-TOF) found: 1228.6770. C₇₈H₉₆N₆O₃Zn requires 1228.6835 [M]⁺. UV-Vis (CH₃CN) λ_{max} (lgε) nm: 414 (5.28). ¹H NMR (CDCl₃, 298 K) δ_H ppm: 0.98 t (6H, ³J=7.1 Hz), 0.99 t (6H, ³J=7.1 Hz), 1.52–1.60 m (10H), 1.70–1.80 m (8H), 2.16–2.25 m (10H), 2.45 s (6H), 2.61 s (6H), 3.13 br.t (2H, ³J_{obs}=4.5 Hz), 3.23 br.s (2H), 3.33–3.60 m (8H), 3.65 br.t (2H, ³J_{obs}=5.3 Hz), 3.93–4.02 m (8H), 4.20 t (2H, ³J=6.1 Hz), 5.49 br.s (1H), 5.91 br.s (1H), 6.87 d (1H, ³J=7.3 Hz), 6.93 t (1H, ³J=7.3 Hz), 7.14 d (1H, ³J=7.2 Hz), 7.27 d (1H, ³J=8.7 Hz), 7.31–7.40 m (5H), 7.70–7.80 m (2H), 7.84 d (2H, ³J=8.0 Hz), 8.08 d (2H, ³J=8.0 Hz), 10.14 s (2H) (NH protons were not assigned).

Tetramacrocyclic 7 was isolated as the third compound in the synthesis of *trismacrocyclic 5*. Eluent: CH₂Cl₂–MeOH 200:1. Yield 11 mg (9 %), dark-red solid. *m/z* (MALDI-TOF) found: 2455.42. C₁₅₆H₁₉₀N₁₂O₆Zn₂ requires 2455.35 [M]⁺. ¹H NMR (CDCl₃, 298 K) δ_H ppm: 0.96 t (6H, ³J=7.1 Hz), 0.98 t (18H, ³J=6.9 Hz), 1.56 br.s (16H), 1.75 br.s (16H), 1.84–1.94 m (6H), 2.20 br.s (18H), 2.63 s (12H), 2.67 s (12H), 3.22 t (2H, ³J=5.6 Hz), 3.40–3.78 m (24H), 3.92 br.s (4H), 3.99 br.s (12H), 4.22 br.s (6H), 6.50 d (2H, ³J=7.8 Hz), 6.60 d (2H, ³J=7.3 Hz), 6.82 s (2H), 6.90 t (2H, ³J=7.8 Hz), 7.02 s (2H), 7.19 t (2H, ³J=7.5 Hz), 7.21 t (2H, ³J=7.7 Hz), 7.32–7.52 m (11H), 7.89–8.10 m (8H) (NH protons were not assigned). ¹³C NMR (CDCl₃, 298 K) δ_C ppm: 14.04 (2C), 14.18 (6C), 15.45 (4C), 15.52 (4C), 22.84 (8C), 26.81 (8C), 27.55 (2C), 28.26 (1C), 28.74 (1C), 32.52 (2C), 32.59 (6C), 33.10 (8C), 42.61 (1C), 47.66 (1C), 52.79 (1C), 53.40 (1C), 68.73 (1C), 70.55 (4C), 70.78 (2C), 70.94 (4C), 71.12 (1C), 97.45 (4C), 110.53, 110.81, 111.20, 112.31, 115.31, 115.98, 116.41, 120.19–120.47 m, 129.24, 129.34, 129.49, 133.31, 134.02, 134.11, 134.28, 138.13, 142.63, 143.01, 143.34–143.46 m, 144.82, 146.38, 147.71, 148.18, 148.88, 149.21 (aromatic carbon atoms are not enough characteristic as they possess very close chemical shifts and form complicated multiplets).

Pentamacrocyclic compound 8 was isolated as the fourth compound in the synthesis of trimacrocyclic **5**. Eluent: CH₂Cl₂–MeOH 100:1. Yield 13 mg (9 %), dark-red solid. *m/z* (MALDI-TOF) found: 2823.64. C₁₇₈H₂₁₈N₁₄O₉Zn₂ requires 2823.56 [M]⁺. ¹H NMR (CDCl₃, 298 K) δ_H ppm: 1.00 t (24H, ³J=7.1 Hz), 1.51–1.65 m (20H), 1.72–1.83 m (16H), 2.17 br.s (8H), 2.13–2.28 m (16H), 3.07 br.s (4H), 3.30–3.48 m (24H), 3.57 br.t (4H, ³J_{obs}=4.4 Hz), 3.64 t (8H, ³J=5.4 Hz), 4.00 br.s (16H), 4.20 br.s (8H), 5.80 s (2H), 6.06 s (1H), 6.07 s (1H), 6.33 s (2H), 6.87 d (2H, ³J=8.5 Hz), 7.05 t (2H, ³J=7.5 Hz), 7.13 d (2H, ³J=7.6 Hz), 7.27–7.52 m (20H), 7.86 d (4H, ³J=7.6 Hz), 7.97 d (4H, ³J=7.5 Hz), 10.15 s (4H) (NH were not assigned). ¹³C NMR (CDCl₃, 298 K) δ_C ppm: 14.22 (8C), 15.41 (4C), 15.51 (4C), 22.86 (8C), 26.88 (8C), 27.44 (2C), 27.87 (2C), 28.32 (2C), 32.66 (8C), 33.25 (8C), 42.96 (2C), 49.06 (2C), 49.46 (2C), 68.7 (2C), 70.3–70.9 m (16C), 97.14 (4C) 111.61, 111.88, 113.36, 116.47, 117.27, 118.80, 118.88, 119.34, 119.68, 119.98, 120.46, 120.61, 120.87, 121.17, 128.61, 128.87, 129.42, 136.81, 137.56, 137.99, 141.45, 141.82, 143.14, 143.20, 143.41, 146.31, 147.49, 147.84, 148.05, 148.20, 149.15 (signals of aromatic carbon atoms are not enough characteristic due to line broadening of some signals and impossibility of the identification of some quaternary carbon atoms).

Tetramacrocyclic compound 16. Obtained from zinc porphyrinate **15** (0.3 mmol, 226 mg), cryptand **12** (0.15 mmol, 92 mg) in the presence of Pd(dba)₂ (16 mol%, 14 mg), BINAP (18 mol%, 17 mg), *t*BuONa (0.45 mmol, 43 mg) in 5 ml of dioxane. Eluent: CH₂Cl₂–MeOH 10:1. Yield 68 mg (23 %), dark-red solid. *m/z* (MALDI-TOF) found: 1955.05. C₁₁₈H₁₄₆N₁₂O₆Zn₂ requires 1955.01 [M]⁺. ¹H NMR (CDCl₃, 298 K) δ_H ppm: 0.97 t (12H, ³J=6.8 Hz), 1.49 sextet (8H, ³J=7.0 Hz), 1.63 quintet (8H, ³J=6.2 Hz), 2.01–2.14 m (12H), 2.34 br.s (8H), 2.56 s (12H), 3.15–3.46 m (24H), 3.31 s (12H), 3.36 s (12H), 3.47–3.65 m (16H), 6.76–6.80 m (4H), 7.30–7.85 m (10H), 7.90–7.96 m (4H).

Tetramacrocyclic compound 17. Obtained from zinc porphyrinate **15** (0.348 mmol, 262 mg), cryptand **13** (0.174 mmol, 115 mg) in the presence of Pd(dba)₂ (16 mol %, 16 mg), DavePhos (18 mol %, 12 mg), *t*BuONa (0.522 mmol, 50 mg) in 3.5 ml of dioxane. Eluent: CH₂Cl₂–MeOH 10:1. Yield 70 mg (20%), dark-red crystalline powder, m.p. 145–150°C. *m/z* (MALDI-TOF) found: 1998.99. C₁₂₀H₁₅₀N₁₂O₇Zn₂ requires 1999.03 [M]⁺. UV-Vis (CH₃CN) λ_{max} nm (lgε): 409 (5.49). ¹H NMR (CDCl₃, 298 K) δ_H ppm: 0.97 t (12H, ³J=7.2 Hz), 1.52 sextet (8H, ³J=7.1 Hz), 1.67 quintet (8H, ³J=6.9 Hz), 2.11 quintet (8H, ³J=6.6 Hz), 2.19 quintet (4H, ³J=6.4 Hz), 2.34 br.s (8H), 2.50 s (12H), 2.87 br.s (8H), 3.00 br.s (8H), 3.23–3.51 m (12H), 3.35 s (24H), 3.69 br.s (4H), 3.79 br.s (4H), 3.86 t (4H, ³J=7.6 Hz), 6.70 br.s (4H), 6.96 br.s (4H), 7.32–7.40 m (4H), 7.47–7.57 m (4H), 9.35 s (2H), 9.70 s (4H). ¹³C NMR (CDCl₃, 298 K) δ_C ppm: 11.4 (4C), 12.0 (4C), 14.1 (4C), 15.3 (4C), 22.7 (4C), 26.3 (4C), 27.8 (2C), 32.3 (4C), 32.9 (4C), 49.1 (2C), 53.2 (4C), 58.4 (2C), 68.0 (2C), 68.2 (4C), 69.1 (4C), 69.6 (2C), 70.0 (2C), 95.8 (2C), 96.6 (4C), 113.3, 119.6, 121.7, 125.5, 126.0, 127.8, 129.9, 135.4, 137.7, 140.8, 145.0, 146.6, 147.4, 147.6 (6 quaternary carbon atoms were not assigned, not all quaternary carbon atoms of the porphyrin moiety were integrated).

Tetramacrocyclic compound 19. Obtained from zinc porphyrinate **18** (0.316 mmol, 238 mg), cryptand **14** (0.158 mmol, 100 mg) in the presence of Pd(dba)₂ (16 mol%, 15 mg), DavePhos (18 mol %, 11 mg), *t*BuONa (0.5 mmol, 48 mg) in 2 ml of dioxane. Eluent: CH₂Cl₂–MeOH 10:1. Yield 33 mg (11 %), dark-red solid. *m/z* (MALDI-TOF) found: 1971.03. C₁₁₈H₁₄₆N₁₂O₇Zn₂ requires 1971.00 [M]⁺. ¹H NMR (CDCl₃, 298 K) δ_H ppm: 0.99 t (12H, ³J=7.1 Hz), 1.52 br.sextet (8H, ³J=6.0 Hz), 1.65 br.s (8H), 2.04 br.s (8H), 2.37 br.s (8H), 2.60 s (12H), 3.08 br.s (8H), 3.27–3.60 m (24H), 3.33 s (12H), 3.35 s (12H), 3.66 br.s (8H), 3.78 br.s (4H), 6.46 br.s (2H), 6.85 br.s (2H), 6.93 br.s (2H), 7.13 br.s (2H), 7.29 br.d (2H, ³J_{obs}=7.8 Hz), 7.41 br.s (2H), 7.54–7.62 m (2H), 7.71 br.d (2H, ³J_{obs}=7.5 Hz), 9.65 s (4H), 9.77 s (2H). ¹³C NMR (CDCl₃, 298 K) δ_C ppm: 11.3 (4C), 12.0 (4C), 14.1 (4C), 15.3 (4C), 22.7 (4C), 26.1 (4C), 32.3 (4C), 32.9

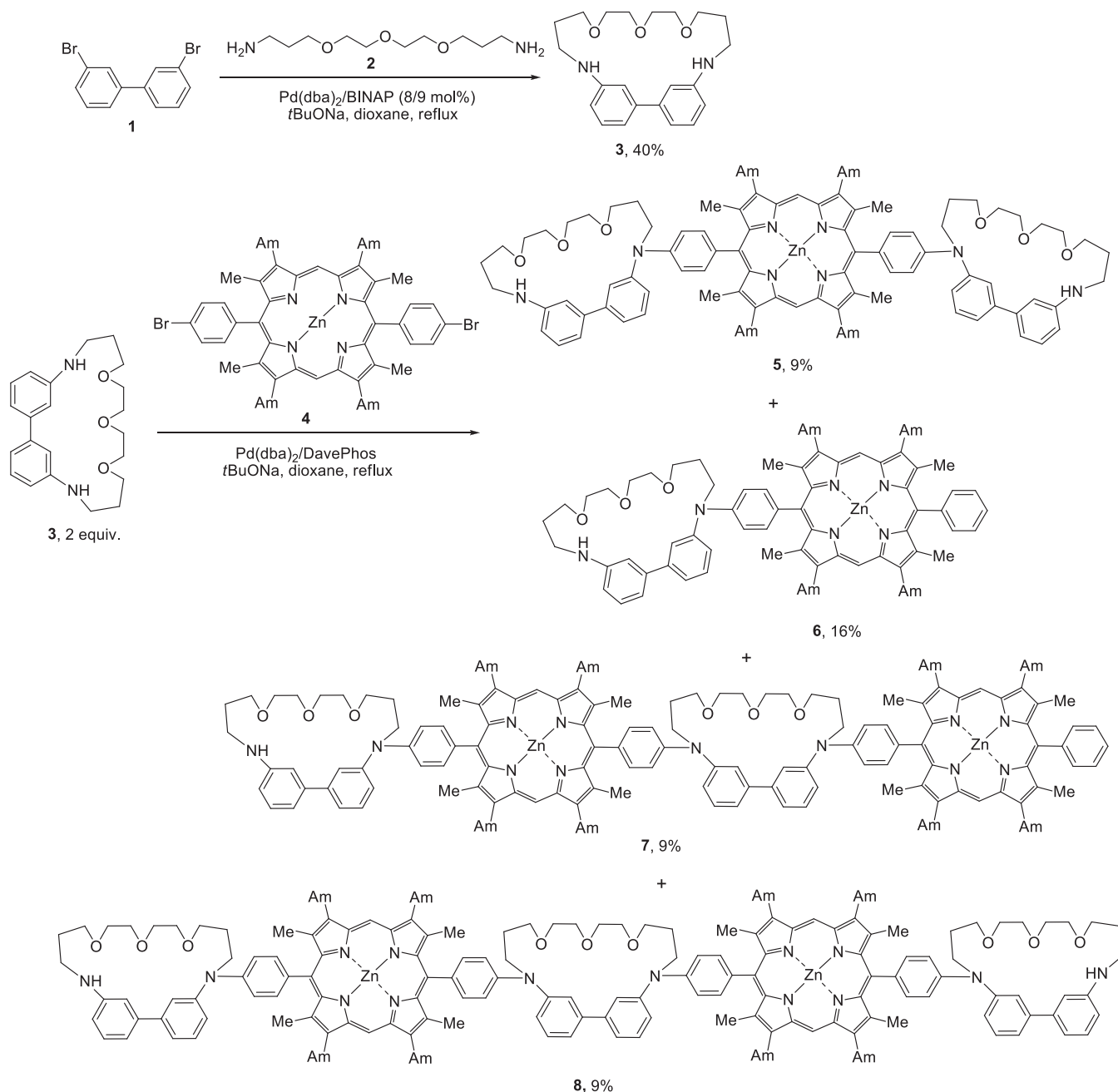
(4C), 51.9 (2C), 52.5 (4C), 58.2 (2C), 67.9–70.6 m (14C), 95.6 (2C), 96.6 (4C), 119.1, 120.2, 121.3, 122.2, 126.7, 127.8, 129.0, 135.3, 137.3, 137.6, 140.7, 145.0, 146.3, 146.5, 146.7, 147.4, 147.7, 148.0 (6 quaternary carbon atoms were not assigned, not all quaternary carbon atoms of the porphyrin moiety were integrated).

Trimacrocyclic compound 20 was isolated as the second compound in the synthesis of tetramacrocyclic **19**. Eluent: CH₂Cl₂–MeOH 5:1. Yield 33 mg (16 %), dark-red crystalline powder. M.p. 147–152 °C. *m/z* (MALDI-TOF) found: 1300.6934. C₇₆H₁₀₀N₈O₇Zn requires 1300.7006 [M]⁺. UV-Vis (CH₃CN) λ_{max} (lgε) nm: 411 (5.32). ¹H NMR (CDCl₃, 298 K) δ_H ppm: 0.98 t (6H, ³J=7.3 Hz), 1.55 sextet (4H, ³J=7.4 Hz), 1.72 quintet (4H, ³J=7.4 Hz), 2.23 quintet (4H, ³J=7.4 Hz), 2.40 br.s (8H), 2.61 s (6H), 2.90 br.s (8H), 3.08 br.s (8H), 3.15 br.s (4H), 3.33 br.s (4H), 3.35 s (4H), 3.45 s (6H), 3.49 s (6H), 3.62 br.t (4H, ³J_{obs}=4.6 Hz), 3.89 t (4H, ³J=5.6 Hz), 6.49 br.s (2H), 6.79 br.s (2H), 7.16 br.s (4H), 7.28 d (1H, ³J=7.7 Hz), 7.56 t (1H, ³J=7.6 Hz), 7.64 s (1H), 7.74 d (1H, ³J=6.9 Hz), 9.70 s (1H), 9.84 s (2H) (NH proton was not assigned).

Results and Discussion

At the first step of our research we synthesized the macrocycle **3** comprising 3,3'-disubstituted biphenyl and trioxadiazine moieties. The synthesis was carried out according to a known procedure,^[24] starting from 3,3'-dibromobiphenyl (**1**) and linear trioxadiazine **2**, in the presence of a standard catalytic system Pd(dba)₂/BINAP (dba=dibenzylideneacetone, BINAP=2,2'-bis(diphenylphosphino)-1,1'-binaphthalene). The target compound was isolated in 40 % yield and introduced in the second catalytic reaction with zinc 5,15-di(4-bromophenyl)porphyrinate **4** (Scheme 1). This coupling was conducted using DavePhos phosphine ligand (DavePhos=2-(dicyclohexylphosphino)-2,2'-dimethylaminobiphenyl) as special experiment revealed the superiority of this donor ligand over more conventional BINAP in the arylation of the secondary amino groups with bromophenyl porphyrinates. It was also important to use Zn(II) complex as free porphyrins often failed to give desired products in similar arylation reactions. The ratio of the starting compounds **3:4** was taken as 2:1, as a result we obtained a series of polymacrocycles: the expected trimacrocyclic **5**, i.e. the product of the diamination of di(bromophenyl) porphyrin, the product of monoamination **6**, and oligomeric tetracyclic and pentacyclic compounds **7** and **8** (Scheme 1). Compounds **6** and **7** were formed in the result of the catalytic amination and catalytic reduction of the C-Br bonds. The isolated yields of all these compounds were small and ranged from 9 to 16 %. The isolation of individual products by chromatography on silica gel was quite tedious and obviously oligomers with higher molecular masses were not obtained in individual state.

Another structural type of porphyrin-containing polymacrocycles is based on the cryptand-like derivatives of diazacrown ethers **12–14**. These compounds were obtained by a previously described method^[25] in sufficient yields (24–38 %) (Scheme 2), they differ by the size of the central diazacrown moiety as well by the nature of the trioxadiazine linker and substitution pattern in the benzyl spacers. Cryptands **12** and **13** were introduced in the Pd(0)-catalyzed diarylation reaction with zinc 5-(4-bromophenyl) porphyrinate **15** (2 equiv.) using the same catalytic system



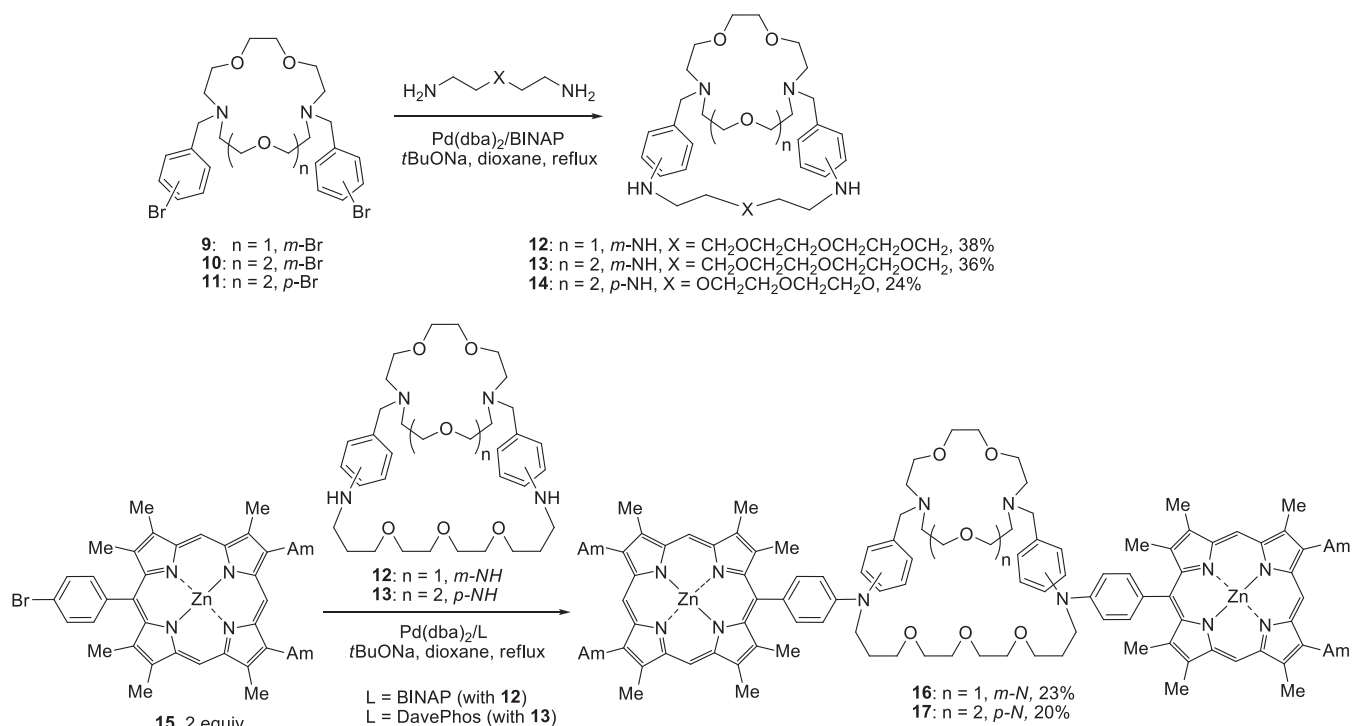
Scheme 1.

$\text{Pd}(\text{dba})_2/\text{DavePhos}$ as in the previous case. As the number of reaction centers decreased in these processes, the target tetramacrocyclic products of diarylation **16** and **17** were isolated in fairly better yields (23 and 20 %, respectively) (Scheme 2). It is interesting that in the case of the reaction of zinc porphyrinate **15** with the cryptand **12** BINAP was found to be also efficient for the coupling.

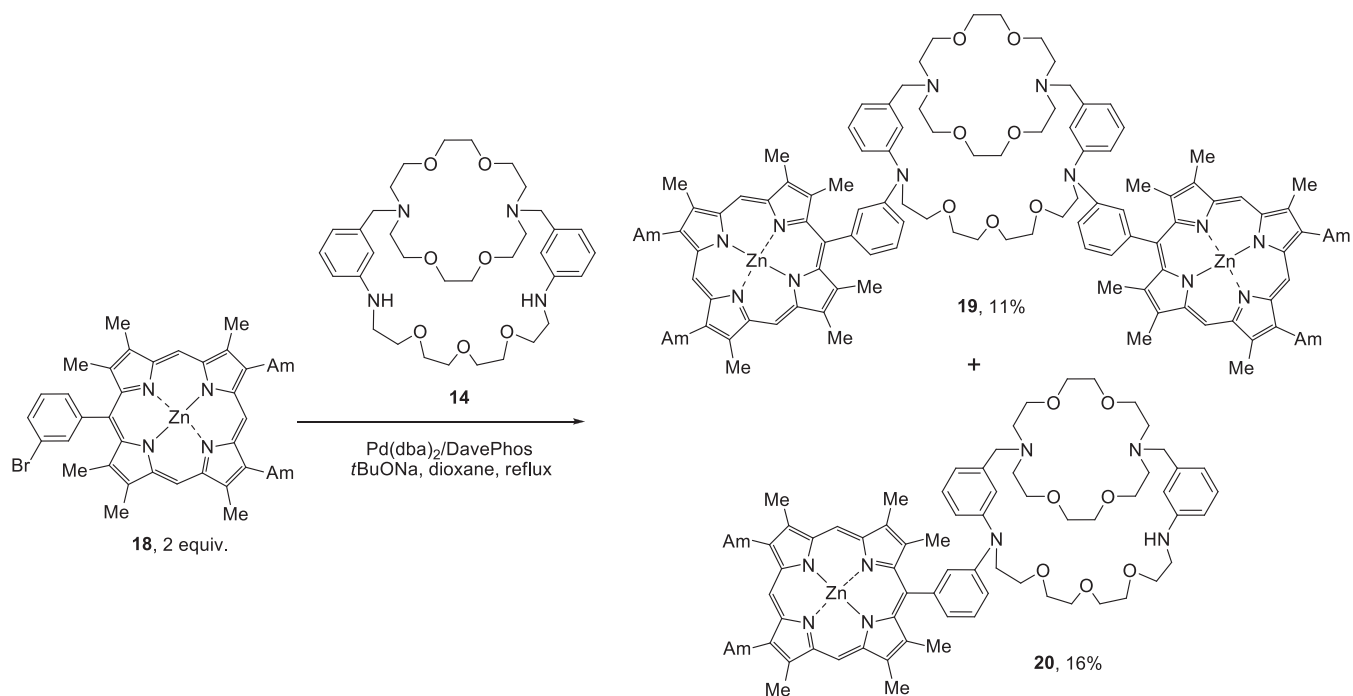
Next we explored the possibility to introduce an isomeric zinc 5-(3-bromophenyl)porphyrinate **18** in the similar reaction with the cryptand **14** (Scheme 3). Porphyrin derivative **18** possesses less active bromine atom compared to its isomer **15** in which bromine is situated in *para*-position to a strong electron-withdrawing porphyrin unit. As expected, the reaction with less reactive zinc porphyrinate **18** resulted in a lower yield of the desired bisporphyrin tetramacrocycle **19** (11 %) while the product

of monoarylation, *i.e.* trimacrocycle **20** was obtained in 16 % yield (Scheme 3).

We investigated the possibilities of polymacrocyclic compounds to act as fluorescent chemosensors for metal cations. In the course of investigation UV-Vis and fluorescent spectra of the polymacrocycles **5**, **6**, **17** and **20** were recorded in MeCN in the presence of 1, 2, 5 equiv. (in some cases also 10, 20, 30 equiv.) of corresponding metal perchlorates: Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Mn(II), Fe(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II), Cd(II), Hg(II), Ag(I), Pb(II). It was found out that the bis-macrocyclic compound **6** could serve as the fluorescent molecular probe for Cu(II), Al(III) and Cr(III) cations because the addition of only these metals led to full quenching of emission (Figure S1). To achieve this full quenching, one needs 2 equiv. of Al(III) (Figure S2), 5 equiv.



Scheme 2.



Scheme 3.

of Cr(III) (Figure S3) or only 1 equiv. of Cu(II). We carried out both UV-Vis and fluorescent titrations (Figures S4, S5) and calculated the stability constants of two complexes with Cr(III): for (6)·Cr(III) complex $\lg K = 6.20 \pm 0.10$ and for (6)·2Cr(III) $\lg K = 12.25 \pm 0.07$. In UV-Vis spectra Cr(III) and Al(III) caused insignificant decrease in the intensity of the absorption band with bathochromic shift by 12 nm while the addition of Cu(II) salt led to a disappearance of this absorption band.

Emission of the *trismacrocyclic* 5 with one central porphyrin and two peripheral diazatrioxamacrocycles is less susceptible to the addition of Cr(III) as only 10 equiv. led to full quenching (Figure S6). However, Cu(II) and Al(III) quench emission efficiently (Figure S7), thus this molecule can be also regarded as a molecular probe for these three cations. The effect of the metal cations on the UV-Vis spectra are quite similar to that of compound 6 (Figure S8).

Tetramacrocyclic ligand **17** can be seen as a chemosensor for Cu(II) cations as only this metal fully quenches its emission upon addition of 10 equiv. (Figures S9, S10). Moreover, this detector is characterized by a low detection limit (0.23 μ M). The stability constant of the complex (**17**)·Cu(II) was found to be equal $\lg K = 5.15 \pm 0.04$ by fluorimetric titration. Trismacrocyclic compound **20** which includes only one porphyrin structural unit and possesses a slightly shorter trioxadiazine linker though selectively responses for Cu(II) cations, is less efficient in detecting this metal as its emission diminishes only 2.5 times after the addition of 15 equiv. of this metal (Figures S11, S12). This fact implies the necessity of fine tuning of the polymacrocyclic structures for increasing selectivity and sensitivity of the detector. In UV-Vis spectra of polymacrocycles **17** and **20** the decrease in the intensity of the absorption maxima upon addition of Cu(II) cations without notable shift was observed (Figures S13, S14).

Conclusions

To sum up, our research revealed the possibility to construct polymacrocyclic compounds incorporating porphyrin and oxaazamacrocyclic structural units using Pd(0)-catalyzed amination reactions. They were tested as potential fluorimetric detectors of metal cations and the strong dependence of the emission quenching in the presence of certain cations on the type and number of macrocycles attached to porphyrin units was firmly established. Two of them (monoporphyrin-based *bis*- and *tris*macrocycles **5** and **6**) were found to be prospective fluorescent detectors for Al(III), Cr(III) and Cu(II) while tetramacrocyclic *bis*porphyrin derivative **17** can serve as the fluorimetric chemosensor for Cu(II).

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