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Dimer of Pd(II) β-Octaethylporphyrin Bound by a 1,3-Butadiene Bridge

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A method for obtaining porphyrin dimers bound by a 1,3-butadiene bridge through homocoupling of 2-boronylethenylporphyrins has been developed. The homocoupling reaction proceeds under mild conditions at room temperature using tetrakistriphenylphosphine palladium as a catalyst in the presence of the oxidizer silver oxide Ag_2O. The corresponding dimeric product was obtained from palladium meso(2-pinacolboronylethenyl)-β-octaethylporphyrinate. The UV-Vis absorption spectrum of the dimeric product is slightly different from that of the monomeric palladium meso-vinyl-β-octaethylporphyrinate, which indicates the absence of π-electronic conjugation between tetrapyrrole aromatic systems. The DFT calculation of the dimer showed that the orthogonal orientation of the butadiene bridge with respect to the plane of tetrapyrrole macrocycles is realized.

Keywords: Porphyrins, porphyrin dimers, homocoupling, pinacol boronates, butadiene link.

Димер Pd(II) β-октаэтилпорфирина, связанный 1,3-бутадиеновым мостиком

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Разработан метод получения димеров порфиринов, связанных 1,3-бутадиеновым мостиком, путем гомосочетания 2-борилэтенилпорфиринов. Реакция гомосочетания протекает в мягких условиях при комнатной температуре при катализе тетракистрифенилфосфинпалладием в присутствии окислителя оксида серебра Ag_2O. Из мезо(2-пинаколборилэтенил)-β-октаэтилпорфирината палладия был получен соответствующий димерный продукт. Электронный спектр поглощения димерного продукта мало отличается от спектра мономерного мезо-винил-β-октаэтилпорфирината палладия, что свидетельствует об отсутствии π-электронного сопряжения между тетрапиррольными ароматическими системами. DFT-расчет димера показал, что в данном случае реализуется ортогональная ориентация бутадиенового мостика по отношению к плоскости тетрапиррольных макроциклов.

Ключевые слова: Порфирины, димеры порфирина, гомосочетание, пинаколборонаты, бутадиеновый мостик.

Introduction

The most advanced technologies are created by nature, so a nature mimic allows us to increase the efficiency of artificial systems and get closer to the perfection of nature. Efforts to create artificial analogs of the natural tetrapyrrolic compounds are an important part of the chemistry.[1] The efficiency of solar energy conversion in the process of photosynthesis is amazing. The key element of the photosynthetic center is a special pair, which is a dimer of bacteriochlorophyll. In an attempt to imitate nature, researchers create many similar dimers of tetrapyrrole compounds. Porphyrin dimers were used in photovoltaics,[2] photocatalytic hydrogen production,[3] in panchromatic photodetectors with near-IR sensitivity.[4] Multiporphyrin palladium complexes were used for the up-conversion of green photons into blue ones.[5] Dimers and oligomers of porphyrins are promising as photosensitizers because they have a higher extinction coefficient in the visible region of the light spectrum.[6] In addition, they are characterized by a large cross-section of two-photon absorption, which allows them to be excited with a near infrared laser.[7,8] This property is especially important for medicine, since radiation in this particular range of spectrum corresponds to the transparency window for the light being the least absorbed by the tissues of the body.[9,10] Therefore, such photosensitizers are promising for photodynamic therapy (PDT) with two-photon absorption.[11]

Recently, methods of cross-coupling catalytic reactions (primarily Suzuki, Sonogashira, Stille reactions) have been widely used for the synthesis of asymmetric dimers and oligomers of porphyrins.[12] Dimerization of arylboronic acids is often a side process in the Suzuki reaction.[13,14] Consistently, the catalytic homocoupling of aryl and vinyl derivatives of boronic acids has become a prospective alternative to dimerization based on the Ullmann and Pshorr reactions catalyzed by copper and other transition metals.[15-20] This process is a very versatile synthetic method, tolerant to most functional groups, and therefore promising as a methodology for obtaining symmetrical functional materials, pharmaceuticals, fine chemical technology products and polymers.[21,22]

However, in contrast to the great number of publications devoted to the Suzuki reaction, very little attention has been paid to the development and study of the arylboronic acid homocoupling reaction. To carry out this reaction, Pd(II) was most often used as a catalyst and air oxygen as an oxidizer.[23-28] Also the catalytic ability of copper salts,[21,29,30] gold,[31,32] and other metals in the dimerization reaction of arylboronic acids is reported. In addition to oxygen, *p*-benzoquinone,[33] electrooxidation,[34] TEMPO in a combination with a Wilkinson rhodium catalyst were also used as an oxidizers,[35] and copper(II) salts were used as an oxidizer during catalysis with ruthenium complexes.[36] A side process of the homocoupling reaction is the oxidation of arylboronic acids to phenols, as well as protodeboration.[26,31] The homocoupling of ethenylboronic acids was practically not researched, but the reaction mechanism was investigated using the example of dimerization of 2-phenylvinylboronic acid, catalyzed by palladium nanoparticles.[37] For porphyrin substrates, there are completely no examples of catalytic coupling with the formation of dyads linked by the 1,3-butadiene bridge. Such compounds were obtained by indirect methods involving several stages. Previously, we developed a method for obtaining asymmetric porphyrin dyads linked by a 2,3-diazabutadiene bridge.[38] Since there have been no methods of dimerization of vinyl substituted porphyrins with the formation of a dimer bound by a butadiene bridge, the task of developing such methods is actual, and this paper shows the possibility of direct catalytic dimerization of boronylethenyl substituted porphyrins obtained in one stage from the corresponding *meso*-vinylporphyrins.

Experimental

General

Reactions were carried out under argon atmosphere using commercially available reagents that were purchased and used as received. Heating reaction vessels was performed with oil bath. Silica gel 40/60 was used for column and flash chromatography. Preparative thin layer chromatography (TLC) was performed using glass plates coated with 5-40 μm silica gel (5 mm thick). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance III 600 MHz spectrometer at 303 K in $CDCl_3$ and CD_2Cl_2. Chemical shifts are reported relative to signals of residual protons of solvents ($CDCl_3$ – 7.26 ppm, CD_2Cl_2 – 5.32 ppm). The assignment of the resonances in the ^{1}H and ^{13}C NMR spectra was achieved by the use of DEPT, COSY and HSQC techniques. The LDI-TOF mass spectra were obtained on a Ultraflex-II mass spectrometer (Bruker Daltonics) in a positive ion mode using reflection mode (20 mV target voltage) without matrix. Electronic absorption spectra were recorded with U-2900 (Hitachi) spectrophotometer in quartz rectangular cells of 10 mm path length.

Synthesis

β-Octaethylporphyrin (OEP) was synthesized by monopyrrole condensation described by Johnson.[39]

Pd(II) 2,3,7,8,12,13,17,18-octaethylporphyrin (PdOEP)[40] was prepared *via* modified procedure of Adler and Longo.[41] $PdCl_2$ (89 mg, 0.50 mmol) was dissolved in heating in 20 mL of DMF and the resulted solution was added to a solution of β-octaethylporphyrin (268 mg, 0.50 mmol) in 10 mL of DMF, then NaOAc (184 mg, 2.24 mmol) was added and the mixture was stirred for 12 hrs at 150 °C. After that the reaction mixture was poured in ice water (0.5 L) and the precipitate was filtered, dissolved in 50 mL CH_2Cl_2, washed with water (2×50 mL), dried over Na_2SO_4, evaporated in vacuum, and the product was purified by flash chromatography with CH_2Cl_2 / petroleum ether (1:1) yielding 303 mg (95 %) of the PdOEP. ^{1}H NMR ($CDCl_3$) δ ppm: 10.14 (4H, s, *meso*-H), 4.09 (16H, m, CH_2), 1.94 (24H, t, J = 7.70 Hz, CH_3). LDI TOF *m/z*: found 639.19, calc. for $[M+H]^+$ $C_{36}H_{45}N_4Pd$ 639.27. UV-Vis (CH_2Cl_2) λ_{max} ($A_{rel.}$) nm: 392 (1.00), 511 (0.08), 545 (0.24).

*Pd(II) 5-formyl-2,3,7,8,12,13,17,18-octaethylporphyrin (**1**)*[42] was obtained via the Vilsmeier-Haack formylation reaction.[43,44] The Vilsmeier reagent, *in situ* formed from 1 mL (11 mmol) of $POCl_3$ and 1 mL (13 mmol) of DMF, was added dropwise to a rapidly stirred solution of 54 mg (0.085 mmol) of PdOEP in 20 mL of dry 1,2-dichloroethane. The resulting mixture was stirred for 2.5 hrs at reflux, then the solvent was evaporated in vacuum and dissolved in 30 mL of CH_2Cl_2, then saturated aqueous solution of Na_2CO_3 and NaOAc was added and the mixture was stirred for 4 hrs. Then the organic phase was separated, washed with water (3×30 mL), dried over Na_2SO_4, evaporated in vacuum and the residue was purified by column chromatography in CH_2Cl_2 / petroleum ether (2:1), yielding 31 mg (55 %) of the target product **1** and 17 mg (30%) of the side product Pd(II) 2-(prop-2-enone-3-yl)-3,7,8,12,13,17,18-heptaethylporphyrin.[45] ^{1}H NMR ($CDCl_3$) δ

ppm: 11.85 (1H, s, CH=O), 9.43 (1H, s, 15-CH), 9.35 (2H, s, 10-CH, 20-CH), 3.82 (4H, q, J = 7.6 Hz, CH_2), 3.79 (12H, m, CH_2), 1.75 (6H, t, J = 7.6 Hz, CH_3), 1.72 (12H, m, CH_3), 1.70 (6H, t, J = 7.6 Hz, CH_3). LDI TOF *m/z*: found 667.29, calc. for $[M+H]^+$ $C_{37}H_{45}N_4OPd$ 667.26. UV-Vis (CH_2Cl_2) λ_{max} ($A_{rel.}$), nm: 397 (1.00), 516 (0.07), 550 (0.16).

*Pd(II) 5-vinyl-2,3,7,8,12,13,17,18-octaethylporphyrin (**2**).* Wittig reagent was prepared as follows: 1.6 M BuLi in hexane (0.19 mL, 0.30 mmol) was added dropwise in stirring to the suspension of triphenylmethylphosphonium iodide (0.1 g, 0.25 mmol) in freshly distilled absolute THF (4 mL), then the mixture was stirred for 10 min till the solution became clear. Pd(II) complex of 5-formyl-*β*-octaethylporphyrin (**1**) (21 mg, 0.031 mmol) was dissolved in absolute THF (5 mL), then the prepared Wittig reagent was slowly added to the solution of **1** in three portions of 0.5 mL after 5 min intervals. After 1 hr of stirring the solvent was evaporated in vacuum, and the residue was dissolved in CH_2Cl_2 (40 mL), washed with water (3×40 mL), dried over Na_2SO_4, evaporated in vacuum, and the product was purified by column chromatography with CH_2Cl_2 / petroleum ether (1:2), yielding 16 mg (76 %) of the product **2**. ^{1}H NMR ($CDCl_3$) δ ppm: 9.93 (2H, br.s, *meso*-H), 9.89 (1H, s, *meso*-H), 9.35 (1H, dd, J_1 = 17.68 Hz, J_2 = 11.06 Hz, C*H*=CH_2), 5.83 (1H, dd, J_1 = 11.06 Hz, J_2 = 1.54 Hz, CH=C*H*$_2$), 4.53 (1H, dd, J_1 = 17.68 Hz, J_2 = 1.54 Hz, CH=C*H*$_2$), 3.88 (16H, m, CH_2), 1.82 (12H, m, CH_3), 1.76 (6H, t, J = 7.70 Hz, CH_3), 1.72 (6H, t, J = 7.70 Hz, CH_3). LDI TOF *m/z*: found 665.24, calc. for $[M+H]^+$ $C_{38}H_{47}N_4Pd$ 665.28. UV-Vis (CH_2Cl_2) λ_{max} ($A_{rel.}$) nm: 400 (1.00), 518 (0.07), 551 (0.14).

*Pd(II) (E) 5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)ethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (**3**).* CuSCN (0.73 mg, 0.006 mmol) and (2-biphenyl)dicyclohexylphosphine (CyJohnPhos) (4.6 mg, 0.013 mmol) were added to 1 mL of absolute 1,4-dioxane and stirred at room temperature for 30 min, then LiO^tBu (4.8 mg, 0.06 mmol), Pd(II) 5-vinyl-2,3,7,8,12,13,17,18-octaethylporphyrin (**2**) (20 mg, 0.030 mmol), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (18.9 mg, 0.12 mmol), bispinacolborane ($(Bpin)_2$) (31 mg, 0.12 mmol) and 2 mL of absolute 1,4-dioxane were consecutively added. The reaction mixture was stirred and refluxed for 15 h, then the solvent was evaporated in vacuum, and the residue was dissolved in 30 mL CH_2Cl_2, washed with water (3×30 mL), dried over Na_2SO_4, evaporated in vacuum, and the product was purified by column chromatography with CH_2Cl_2 / petroleum ether (1:2) yielding 11 mg (46%) of the product **3**. ^{1}H NMR ($CDCl_3$) δ ppm: 10.19 (1H, d, J = 17.5 Hz, Bpin-CH=C*H*), 10.04 (2H, br.s, *meso*-H), 10.00 (1H, s, *meso*-H), 5.68 (1H, d, J = 17.5 Hz, Bpin-C*H*=CH), 4.04 (16H, m, CH_2), 1.89 (12H, m, CH_3), 1.70 (6H, t, J = 7.70 Hz, CH_3), 1.69 (6H, t, J = 7.70 Hz, CH_3). LDI TOF *m/z*: found 791.38, calc. for $[M+H]^+$ $C_{44}H_{58}BN_4PdO_2$ 791.37. UV-Vis (CH_2Cl_2) λ_{max} ($A_{rel.}$) nm: 401 (1), 517 (0.08), 550 (0.14).

*Pd(II) (E) 2-(2,3,7,8,12,13,17,18-octaethylporphyrin-5-yl)-ethenylboronic acid dimethyl ester (**4**).* To a suspension of the pinacol boronate **3** (20 mg, 0.025 mmol) in 0.1 mL of MeOH and 0.1 mL of MeCN a solution of KF (5.8 mg, 0.1 mmol) in 0.03 mL H_2O was added. The reaction mixture was stirred for 10 min, then a solution of tartaric acid (7.7 mg, 0.05 mmol) in 0.1 mL of THF was added and stirred for 1.5 hrs. The precipitate was filtered and dissolved in methanol, then it was purified with flash chromatography in CH_2Cl_2 : petroleum ether = 1 : 1 yielding 12.5 mg (67 %) of the product **4**.

*(E,E) 1,4-bis-(2,3,7,8,12,13,17,18-octaethylporphyrinato palladium(II)-5-yl)buta-1,3-diene (**5**).* $Pd(PPh_3)_4$ (7.6 mg, 0.0066 mmol) was dissolved in 1 mL of THF and freshly precipitated Ag_2O (22 mg, 0.095 mmol) was added to the solution, then the porphyrinylethenyl pinacol boronate **3** (15 mg, 0.019 mmol) was added at stirring. The reaction mixture was stirred and refluxed for 12 hrs, then the solvent was evaporated, the residue was dissolved in CH_2Cl_2 (10 mL) and washed with water (2×10 mL), dried over anhydrous sodium sulfate, evaporated in vacuum and the product was purified with flash chromatography in dichloromethane : petroleum ether = 3 : 7, yielding 10 mg (40 %) of the dimeric product **5**. ^{1}H NMR (CD_2Cl_2) δ_H ppm: 10.16 (4H, s, *meso*-CH), 10.11 (2H, s, *meso*-CH), 9.24 (2H, m, 5^1-CH, $5'^1$-CH), 6.70 (2H, m, 5^2-CH, $5'^2$-CH), 4.05–4.16 (32H, m, CH_2CH$_3$), 1.98 (24H, t, J = 7.9 Hz, CH_2CH_3), 1.98 (12H, t, J = 7.9 Hz, CH_2CH_3), 1.95 (12H, t, J = 7.9 Hz, CH_2CH_3), 1.66 (12H, t, J = 7.8 Hz, CH_2CH_3). LDI TOF *m/z*: found 1328.3, calc. for M^+ $C_{76}H_{90}N_8Pd_2$ 1328.54. UV-Vis (CH_2Cl_2) λ_{max} ($A_{rel.}$) nm: 410 (1.00), 520 (0.13), 552 (0.18).

*X-Ray diffraction study of **4***

Compound **4** was crystallized from methanol to give two polymorphic forms of dark red crystals **4a** and **4b**. Single-crystal X-ray data of the crystals of **4a** and **4b** were collected using Bruker KAPPA APEX II automated four-circle area detector diffractometer (MoKα radiation). The unit cell parameters were refined using the whole datasets. The experimental intensities were corrected for the absorption using the SADABS program.[46] The structures were determined by the direct method (SHELXS97)[47] and refined by the full-matrix least-squares method (SHELXL-2018/3)[48] on F^2 for all data. The structure of the **4a** was refined in the anisotropic approximation for all non-hydrogen atoms, the structure of **4b** was refined in the anisotropic approximation for the Pd atom and isotropic for the remaining atoms. The hydrogen atoms were placed at geometrically calculated positions. The main crystallographic data and characteristics of the X-ray diffraction experiment are given in Table 1.

Table 1. Crystallographic data and details of data collection.

Compound	**4a**	**4b**
Empirical formula	$C_{40}H_{51}BN_4O_2Pd$	$C_{40}H_{51}BN_4O_2Pd$
M	737.05	737.05
T, K	100(2)	100(2)
Crystal size, mm	0.16 × 0.12 × 0.06	0.36 × 0.08 × 0.01
Crystal system	triclinic	triclinic
Space group	P–1	P–1
a, Å	8.4934(5)	10.193(7)
b, Å	14.7906(9)	12.692(8)
c, Å	14.8234(9)	14.926(11)
α, °	89.260(2)	99.11(4)
β, °	82.701(2)	93.78(4)
γ, °	75.023(2)	109.06(3)
V, Å^3	1783.93(19)	1788(2)
Z	2	2
$\rho_{calc.}$, g/cm^3	1.372	1.369
μ(MoK_α), mm^{-1}	0.561	0.560
$2\theta_{max}$, grad	60	50
No. of observed / independent reflections	26437/10128	20753/6119
No. of independent reflections with $I > 2\sigma(I)$	7037	1624
No. of refined parameters	433	198
$R(F)$; $wR(F^2)$ [$I > 2\sigma(I)$]	0.0536; 0.0860	0.1308; 0.2257
$R(F)$; $wR(F^2)$ [all data]	0.0909; 0.0992	0.3829; 0.3422
GOOF	1.026	0.935
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e·Å^{-3}	0.861; –1.280	0.875; –1.286

The coordinates of the atoms are deposited in the Cambridge Crystallographic Data Center, CCDC numbers 2206766 (**4a**), 2206767 (**4b**). X-Ray diffraction experiments were performed using the equipment of the Center for the collective use of physical methods at the A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences.

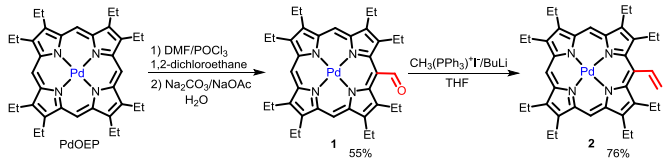
Quantum-chemical calculations

Quantum-chemical calculations of geometry and electronic structure were made with the software package Gaussian 09W[49] using density functional theory (DFT) method with the hybrid correlation-exchange functional B3LYP. A full-electron 6-31G(d,p) basis set was used for the geometry optimizations, electrons of palladium atoms were rendered by the basis set with an effective potential for internal electrons LaNL2DZ. The molecules were calculated in dichloromethane solution using the polarized continuum (PCM) model. The starting geometry of **5** was constructed from the geometry of **4a** obtained using X-ray diffraction study, taken without the boronic substituent and dimerized. S-*cis* and s-*trans* conformations of the 1,3-butadiene bridge with *E,E*-configuration were used for the geometry optimizations and the most stable s-*trans* conformation was found and chosen.

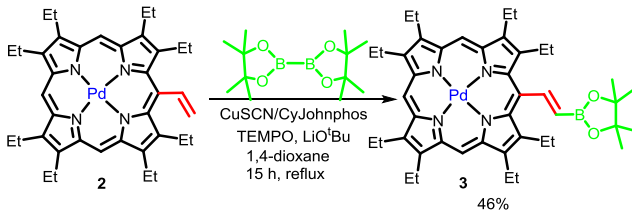
Results and Discussion

As a starting compound *β*-octaethylporphyrin (OEP) being one of the most used model porphyrins, along with *meso*-tetraphenylporphyrin, was chosen as the primary substrate for the synthesis. It was metallized with palladium. It is known that the palladium complex of *β*-octaethylporphyrin (PdOEP) possesses a high quantum yield and a long lifetime of phosphorescence and a triplet excited state. This property led to its use as a triplet photosensitizer.[50] However, a sufficiently short-wave irradiation is required to excite it, which does not meet the requirements of PDT. For PDT, it is necessary to excite the photosensitizer with radiation with a wavelength in the area of tissue transparency, *i.e.* red and near-infrared light. Dimerization of porphyrin makes it possible to use two-photon excitation by longer-wavelength radiation.[51]

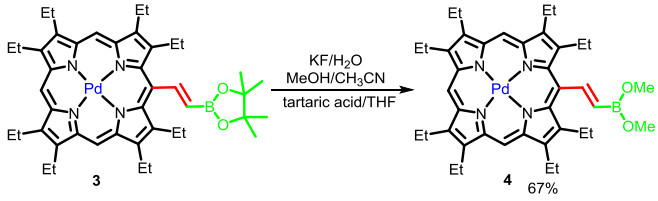
In order to synthesize palladium *β*-octaethylporphyrin dimer bound by the 1,3-butadiene bridge, a corresponding monomer, palladium *meso*-vinyl-*β*-octaethylporphyrin was obtained. To achieve this, the starting palladium complex PdOEP was first formylated with the Vilsmeier–Haack formylation reaction,[42,44,52] and on the second stage the *meso*-formyl product **1** was introduced into the Wittig reaction with methyltriphenylphosphonium iodide to produce the palladium *meso*-vinyl-*β*-octaethylporphyrin **2** with 76 % yield (Scheme 1).



Scheme 1. Preparation of the palladium *meso*-vinyl-*β*-octaethylporphyrin (**2**) from PdOEP.



Scheme 2. Synthesis *of meso*-(2-borylethenyl)-*β*-octaethylporphyrin (**3**).



Scheme 3. The pinacol boronate trans-esterification with methanol.

The obtained vinyl derivative **2** was borylated at the beta position of the vinyl group by the method of direct bispinacolborane borylation using copper complex catalysis previously developed by us.[53] The borylation of **2** proceeded smoothly yielding palladium complex of *meso*-(2-borylethenyl)-*β*-octaethylporphyrin **3** with 46 % yield (Scheme 2).

The pinacol boronate *trans*-esterification with methanol was performed directly from **3** producing the corresponding methyl boronate ester **4** with 67 % yield (Scheme 3).

The methyl boronate **4** was crystallized from methanol leading to two crystal polymorphs **4a** and **4b**. Their structures were determined using X-ray diffraction analysis. The crystal lattice of both polymorphs is triclinic, the symmetry group is P-1. The palladium atom of the complexes is located in the plane of the porphyrin ring. The exocyclic double C=C bond has *E*-configuration and is orthogonal to the porphyrin core, which excludes the π-electronic conjugation between them. The distance between the Pd atom and the N atoms is 2.016–2.022 Å which is close to the standard values. The structures of the molecules in **4a** and **4b** differ in the conformation of two ethyl groups (Figure 1).

The crystal packing of compound **4a** has a feature that is manifested by the presence of a shortened unit cell parameter equal to 8.5 Å. This means that there are quite strong intermolecular interactions between molecules bound by translation along this parameter, binding them into stacks (Figure 2). If we construct the root-mean-square planes for porphyrin macrocycles, then the distances between them in stacks will be 3.344 Å. The distance between the centers of the rings is 3.772 Å, and the shift of the centers is 1.745 Å. It is fundamentally important that *β*-ethyl substituents have practically no effect on the formation of such stacks. At the same time, polymorphic modification **4b** lacks similar intermolecular interactions.

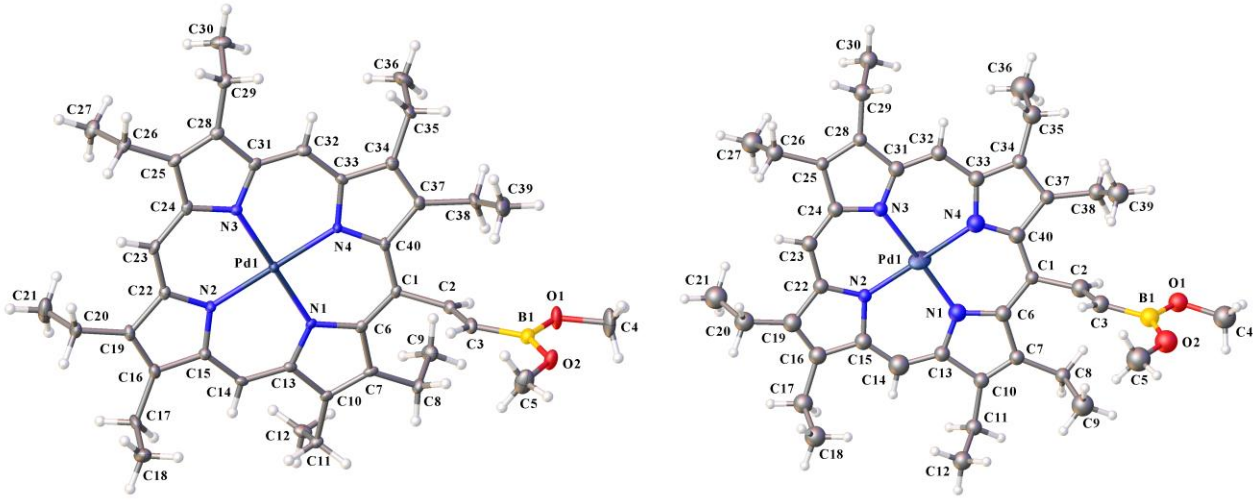


Figure 1. The structure of the molecules of polymorphs **4a** and **4b**.

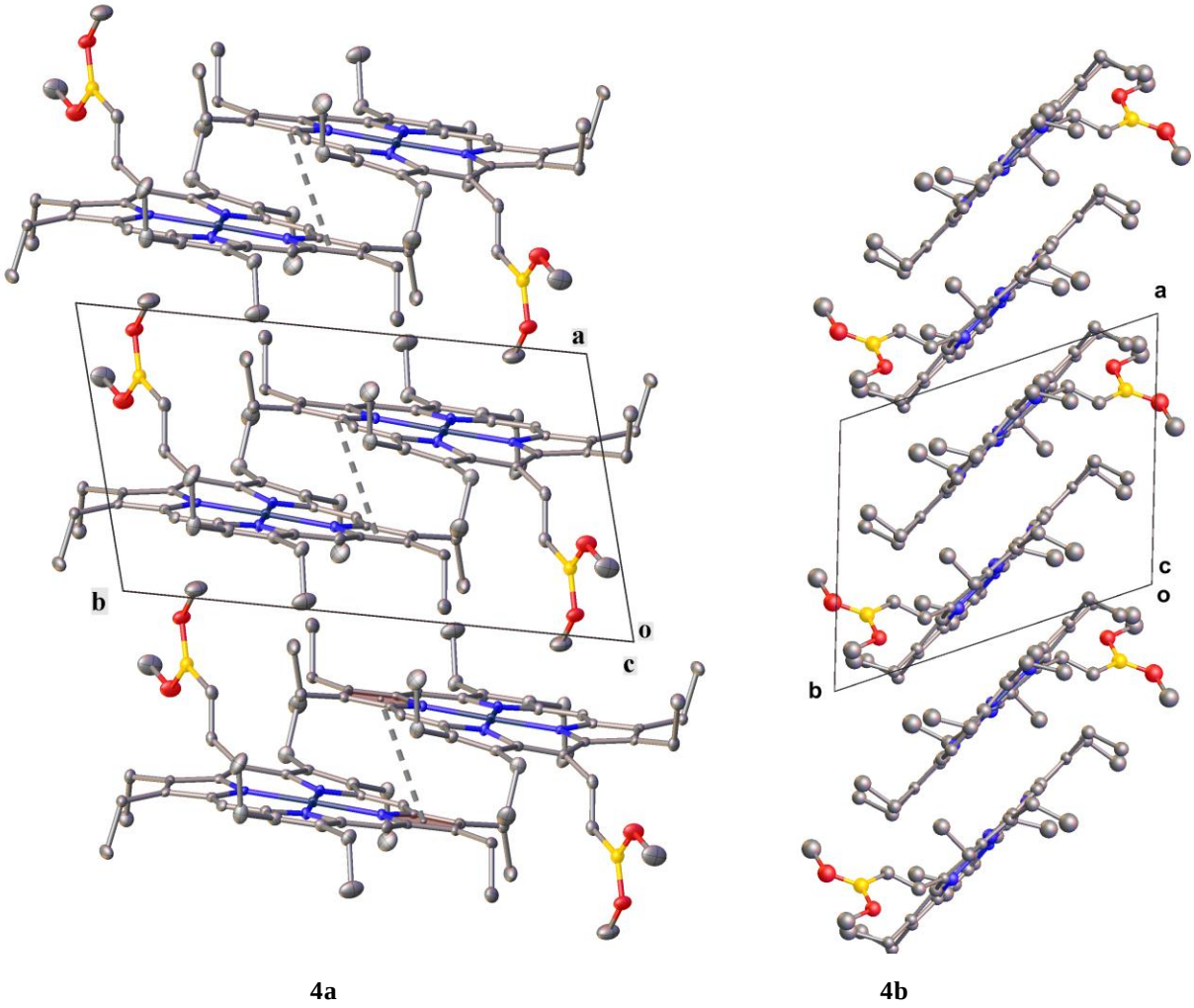
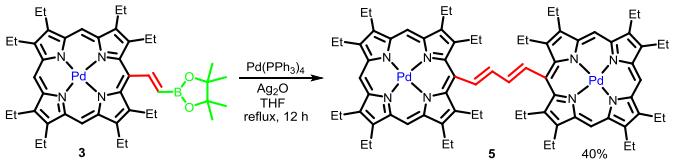


Figure 2. Fragments of crystal packages of crystals **4a** and **4b**.



Scheme 4. The scheme of the palladium catalyzed homocoupling of the 2-porphyrinylethenyl pinacol boronate **3**.

The obtained porphyrin based ethenylboronic derivative **3** is a nucleophilic substrate of the Suzuki cross-coupling, and the homo-coupling of the nucleophilic substrate obviously needs an oxidant. Optimization of homo-coupling reaction conditions led to the choice of silver oxide Ag_2O as an oxidant which was also used as a base. The reaction proceeded when heated in THF leading to the dimeric product **5** with 40 % yield (Scheme 4). The low yield is presumably associated with parallel processes of degradation of the boronic derivative: protodeboration, hydrolysis, oxidation.[54-56] The homocoupling does not occur in the absence of palladium, which thus plays the role of the catalyst.

The structure of the resulting porphyrin dimer **5** was confirmed by NMR spectroscopy (Figure 3). The proton NMR spectrum of the product contains characteristic multiplets of CH-protons of the AA'XX' diene system with a large J^3 constant of *ca*. 18 Hz, characteristic of *trans*-ethene protons. The signals of α-protons close to porphyrin are shifted to a low field due to the ring current of the tetrapyrrole macrocycle and are at 9.24 ppm, while the multiplet of more distant β-protons is at 6.70 ppm. Compared with the spectrum of the "monomer" – *meso*-vinylporphyrin, the α-proton signals are slightly shifted (~0.1 ppm), and the β-proton signals are for 0.9 ppm shifted to a low field due to the de-shielding effect of the vinyl substituent that has appeared. The signals of the β-octaethylporphyrin system are shifted within 0.2 ppm. In the LDI mass spectrum of the product, a molecular ion with *m/z* = 1328.3 is observed, corresponding to the mass of the dimer **5**.

The UV-Vis spectrum of **5** contains a Soret band at 410 nm and Q bands at 520 nm and 552 nm. The spectrum differs appreciably from the spectra of the monomer **2** and the boryl precursor **3**, both the latter being practically identical (Figure 4). The similarity of the spectra of **2** and **3** stems from the total absence of π-electron conjugation of the exocyclic double bond with the tetrapyrrole macrocycles due to their orthogonal orientation, confirmed in the X-ray structure of the methyl boronate derivative **4**. Bathochromic shift of the absorption bands of the dimer **5** is obvious (10 nm for the Soret band and a little for the Q bands). A relatively weak change in the spectrum indicates rather a lack of π-electron coupling between macrocycles, which could be the consequence of the almost orthogonal orientation of the plane of the butadiene bridge with respect to the plane of the porphyrin ring as in **2** and **3**. In order to study the structure of the dimer molecule, quantum chemical calculations were performed using the DFT method. Optimization of the geometry of the molecule by the B3LYP/6-31G(d,p) method in dichloromethane led to the most stable conformation in which coplanar porphyrin rings are shifted relative to each other, and thus oriented according to the type of *J*-aggregates (Figure 5). This type of the relative configuration of the tetrapyrrole macrocycles can be responsible for the slight bathochromic shift of the Soret band according to the observations of spectra of *J*-aggregates.[57] An alternative cofacial conformation was also found in the geometry optimizations and there was a π-electronic coupling of porphyrin systems with a butadiene bridge. The conjugation became possible because the angle of rotation of the bridge was changed from 90 to about 45 degrees. At the same time, there was a significant distortion of the porphyrin cycle. The energy of such a conformation was 15 kcal/mol higher. The calculation of electronic transitions by the TD-DFT method showed that the spectrum of the non-conjugate conformation practically does not much differ from the spectrum of the monomer, and the conjugate has a spectrum dramatically shifted to the bathochromic region. Thus, based on the available experimental and calculated data, it can be concluded that there is an unconjugated dimer conformation in the solution with the relatively shifted porphyrin rings by the type of *J*-aggregates.

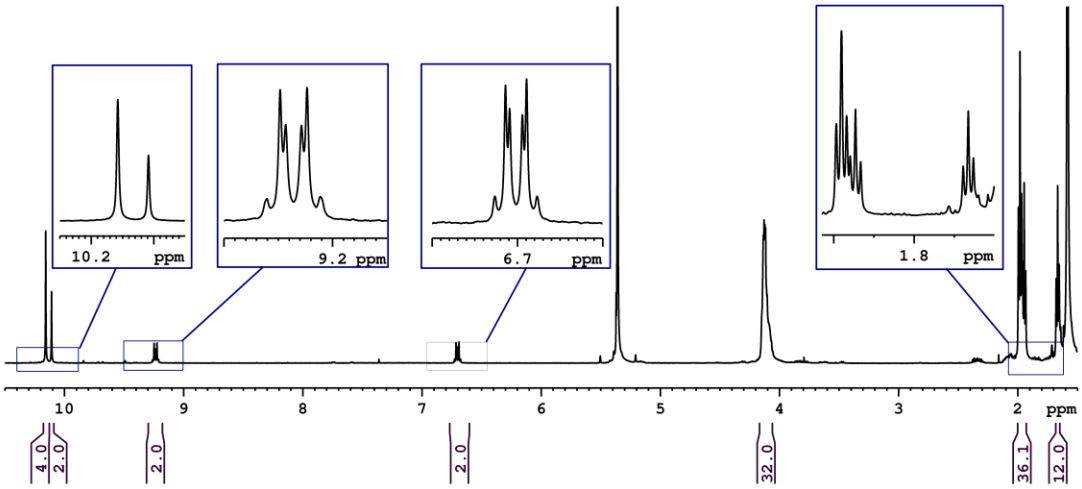


Figure 3. ^{1}H NMR spectrum of the dimer **5**.

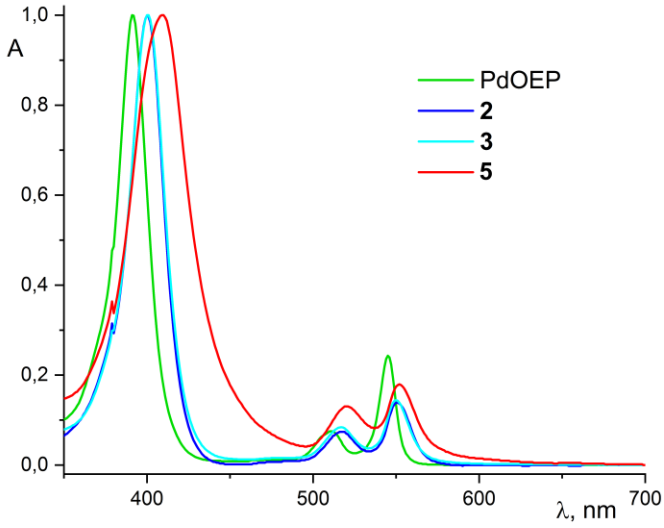


Figure 4. UV-Vis spectra of the dimer **5**, and its precursors **2**, **3**, PdOEP.

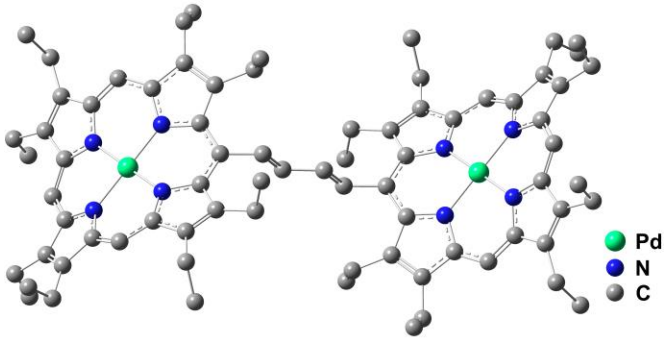


Figure 5. Geometry of the dimer **5** optimized by the DFT (B3LYP/6-31G(d,p)). Hydrogen atoms are omitted for clarity.

In conclusion, a new method of homocoupling of 2-boronylalkenyl-substituted porphyrins, leading to the dimer in which the porphyrin macrocycles are connected by the 1,3-butadiene bridge, has been elaborated. The complete functionalization strategy of the initial unsubstituted porphyrins leads to the dimer in only 4 stages, starting with Vilsmeier–Haack formylation followed by the Wittig reaction leading to the vinylporphyrin monomer. The vinylporphyrins thus obtained can be dimerized in two stages, using the developed homocoupling method, including catalytic CH-borylation. The UV-Vis spectrum and DFT calculations of the dimer showed the absence of the conjugation between tetrapyrrole macrocycles due to the orthogonal orientation of the butadiene bridge relatively to the macrocycle planes.

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