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A panchromatic pyrazine-fused porphyrin dimer

Inna A. Abdulaeva,[a] Daria A. Polivanovskaia,[a] Kirill P. Birin,*[a] Yulia G. Gorbunova[a,b] and Aslan Yu. Tsivadze[a,b]

[a] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation. E-mail: kirill.birin@gmail.com*

[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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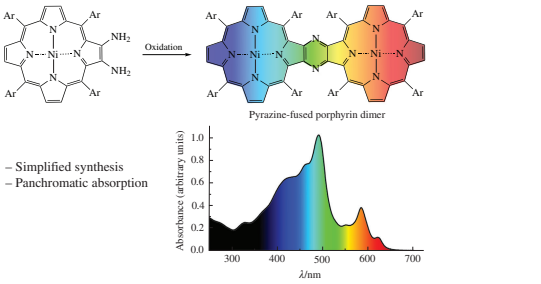
New pyrazine-fused porphyrin dimer was unexpectedly produced by mild oxidation of [2,3-diamino-5,10,15,20-tetrakis(4-butoxyphenyl)porphyrinato]nickel(II) in 40% yield. The obtained porphyrin dimer demonstrates bathochromic shift of absorption bands compared to the reported analogues, along with panchromatic absorption in the 250–650 nm range, which is promising for optical, photovoltaic and medical applications.



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Porphyrins are organic dyes with exceptional absorption and luminescence characteristics, which originate from their extended aromatic system embracing the whole tetrapyrrole macroheterocycle and determine their multiple applications in modern science, such as solar energy conversion, optical limiting, non-linear optics, sensing and molecular recognition.[1] Fine tuning of their physical and chemical properties requires a modification of the porphyrin electronic structure, which is related to the value of the frontier orbitals energy gap.

One of the approaches to control over the aromatic system of porphyrins is an expansion of their π-system through fusion of peripheral aromatic moieties. Thus, benzo-annulation allowed the modification of the spectral and electrochemical properties of the resulting porphyrins.[2–4] In general, this modification caused the decrease in the HOMO–LUMO energy gap and consequently led to the bathochromic shift of absorption bands as well as to the decrease in the redox potentials.

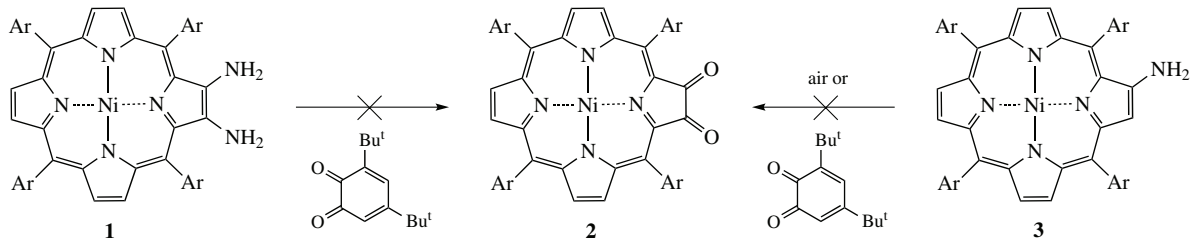
Further expansion of the porphyrin aromatic system was achieved by the construction of porphyrin dimers using the conjugated fused moieties. The benzo-fused diporphyrins demonstrate bathochromic absorption shifts[5,6] and possess absorption spectra similar to the ones of bacteriochlorins as promising dyes for multiple optical applications.[7–9] However, a significant drawback of the benzo-annulation products consists in their low chemo- and photostability, which in turn promotes the search for heterocyclic analogues. The pyrazine- and quinoxaline-appended porphyrins proved to be stable and readily available[10,11] as vell as revealed promising physical and chemical properties.[12,13] Porphyrin oligomers bearing a tetraazaanthracene connection have been also synthesized in a similar way.[14,15]

The decrease in the size of connection moiety results in stronger interaction between the porphyrin parts in the dimeric molecule. For this reason, pyrazine-fused diporphyrins, which are accessible by two general approaches,[16–20] look promising. The first method for their preparation consists in the condensation of diaminoporphyrins and dioxochlorins,[17] whereas the second one is based on the oxidative dimerization of 2-aminoporphyrins.[16,19,20] The latter is typically performed by use of DDQ in $CHCl_3$ or trifluorotoluene in the presence of TFA and affords the target dimer in yields of 4–97% depending on the origin of porphyrin substrate and the reaction conditions. Note that the oxidation of 2-(phenylamino)porphyrin under similar conditions provides piperazine-fused analogue.[21] Interestingly, pyrazine-fused dimer was also formed in the Ullmann coupling of 2-amino-3-bromoporphyrin.[18] All the reported pyrazine-fused porphyrin dimers were found to possess significant absorption in the red spectral range along with panchromatic absorption in the 300–650 nm range, which is of importance for optical and medical applications. Nevertheless, the complexity of the synthesis implying specific conditions for the oxidation of 2-aminoporphyrins should be mentioned as a considerable disadvantage.

Another approach for tuning the optical properties of porphyrin dimers is the introduction of electron-donor groups to the peripheral substituents, which is expected to shift the absorption bands bathochromically. In this work, we focused on the search for approaches to the pyrazine-fused porphyrin dimers bearing electron-donor substituents at *meso*-positions of the macrocycle using 5,10,15,20-tetrakis(4-butoxyphenyl)porphyrin as a model compound. First, we attempted to prepare the corresponding 2,3-diamino- and 2,3-dioxoderivatives for their further condensation by analogy with the known procedure.[17]

Recently we reported on the transformation of nickel(II) 2,3-diaminoporphyrin bearing bulky mesityl groups involving its selective oxidation into 2,3-dioxochlorin using 3,5-di-*tert*-butyl-*o*-quinone.[22] In a similar way, we tried to oxidize diamine **1** into dione **2** (Scheme 1),[†] however, the complete degradation of the starting material was observed. The oxidation of 2-amino-porphyrin **3** using *o*-quinone or air[23,24] also did not allow the preparation of quinone **2**.

[†] Starting aminoporphyrins **1** and **3** were prepared by the reduction of corresponding nitroporphyrins following our published procedures[22] and used in further stages immediately without isolation.



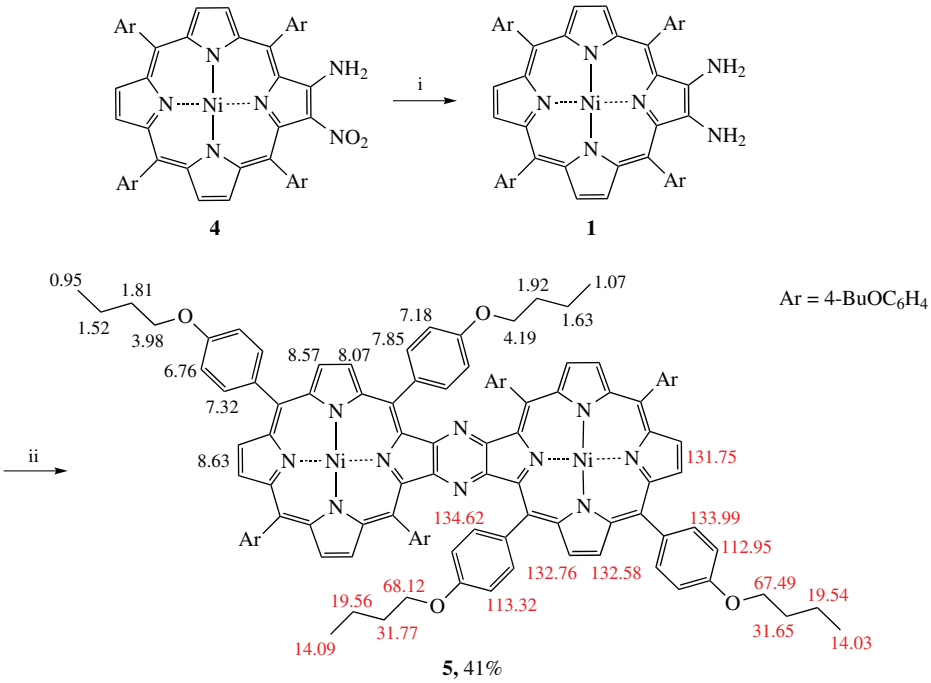
Ar = 4-BuOC$_6$H$_4$

Scheme 1

In this respect we attempted to oxidize diamine **1** in air under mild conditions. Compound **1** was obtained by reduction of 2-nitro-3-aminoporphyrin **4** (Scheme 2),[22] and its fresh solution in CH_2Cl_2 was passed through a column packed with silica unexpectedly affording pyrazine-fused porphyrin dimer **5** in 16% yield. We suppose that the mechanism of this transformation implies *in situ* formation of the corresponding 2,3-dioxochlorin followed by its immediate condensation with diamine **1**. This assumption is in conformity with the reported synthesis of a similar dimer.[17] Slight modification of the procedure allowed us to improve the yield of compound **5**. Stirring the CH_2Cl_2 solution of compound **1** in air followed by flash chromatography on silica provided dimer **5** in 25% yield. In turn, stirring of the CH_2Cl_2 solution of diamine **1** in air in the presence of silica with TLC control and further chromatographic separation gave compound **5** in 41% yield (see Scheme 2).‡

The obtained dimeric Ni(II) porphyrin **5** possesses panchromatic absorption in 250–650 nm range, which is not typical for tetraarylporphyrins but was observed for pyrazine-fused porphyrin dimers[16,17,19,20] (Figure 1). The significant broadening and bathochromic shift of the absorption bands in the spectra of these diporphyrins originate from the deviation of their molecules from planarity resulting in the distortion of aromatic system.

The comparison of the UV-VIS spectral data of pyrazine-fused porphyrin dimers bearing different *meso*-aryl substituents



Ar = 4-BuOC$_6$H$_4$

Scheme 2 *Reagents and conditions*: i, $NaBH_4$, Pd/C, CH_2Cl_2, MeOH; ii, air, silica, CH_2Cl_2. The assignment of principal ^{1}H (top) and ^{13}C (bottom) signals in structure **5** is provided.

‡ *Compound* **5**. A mixture of 2-nitro-3-aminoporphyrin **4** (51 mg, 0.05 mmol) and Pd/C (10%, 50 mg) in CH_2Cl_2 (16 ml) and MeOH (0.6 ml) was purged with argon for 3 min. Sodium borohydride (29 mg, 0.75 mmol) was added portionwise over 10 min. After complete consumption of the starting material (TLC), the mixture was filtered through Celite 545 under argon, evaporated and passed through a short pad of silica using hexane–CH_2Cl_2 mixture (3 : 2) → pure CH_2Cl_2 as eluent. The obtained diamine **1** was dissolved in CH_2Cl_2 (10 ml), then silica (100 mg) was added and the mixture was stirred in air at ambient temperature overnight. The reaction mixture was concentrated and the residue was purified by flash chromatography through a pad of silica using hexane–CH_2Cl_2 (3 : 2 → 2 : 3). The evaporation of the appropriate fractions provided 20 mg (41%) of product **5**. ^{1}H NMR (600 Hz, $CDCl_3$) δ: 8.63 (s, 2H, H$_\beta$), 8.57 (d, 2H, H$_\beta$, ^3J 4.8), 8.07 (d, 2H, H$_\beta$, ^3J 4.8), 7.85 (br. s, 4H, H$_{o\text{-}C_6H_4}$), 7.32 (br. d, 4H, H$_{o\text{-}C_6H_4}$, ^3J 8.2 Hz), 7.18 (d, 4H, H$_{m\text{-}C_6H_4}$, ^3J 8.3 Hz), 6.76 (d, 4H, H$_{m\text{-}C_6H_4}$, ^3J 8.3 Hz), 4.19 (t, 4H, CH_2O, ^3J 6.5 Hz), 3.98 (br. t, 4H, CH_2O, ^3J 6.5 Hz), 1.92 (quintet, 4H, CH_2, ^3J 6.7 Hz), 1.81 (quintet, 4H, CH_2, ^3J 6.6 Hz), 1.63 (sextet, 4H, CH_2, ^3J 7.4 Hz), 1.52 (sextet, 4H, CH_2, ^3J 7.4 Hz), 1.07 (t, 6H, Me, ^3J 7.4 Hz), 0.95 (t, 6H, Me, ^3J 7.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 159.26, 158.32, 147.60, 145.08, 142.07, 140.76, 134.62, 134.00, 132.76, 132.58, 132.36, 131.98, 131.75, 131.43, 120.38, 115.78, 113.32, 112.95, 68.12, 67.49, 31.77, 31.65, 19.56, 19.54, 14.09, 14.03. For assignment of some signals, see Scheme 2. MS (MALDI-TOF, *m/z*: 1940.90 $[M]^+$ (calc. for $C_{120}H_{116}N_{10}{}^{58}Ni_2O_8$, *m/z*: 1940.77). UV-VIS ($CHCl_3$) λ_{max}/nm (log ε): 329 (4.54), 424sh, 491 (5.12), 585 (4.76), 622 (4.25).

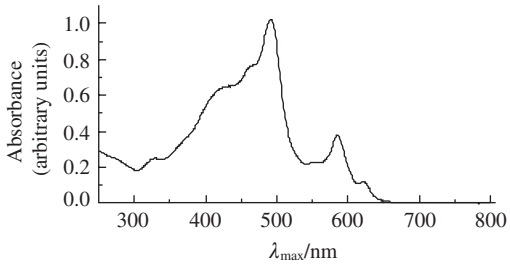


Figure 1 UV-VIS spectrum of compound **5** in $CHCl_3$.

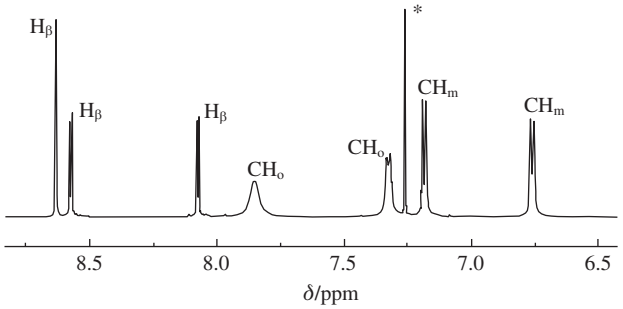


Figure 2 Aromatic region of the ^{1}H NMR spectrum of complex **5** in $CDCl_3$.

clearly indicates that the absorption maxima are gradually red shifted upon growth of the sterical hindrance of these *meso*-substituents (Table 1). This cat be reasonably explained by the increase in the distortion of the aromatic system at the pyrazine junction point. Note, that the prepared dimer **5** reveals the most red-shifted absorption compared with the reported phenyl-substituted analogue.[17] Along with the sterical effect of substituents in aryl groups, we predominantly attribute this shift to the influence of multiple electron-donor alkoxy substituents, which typically decrease the porphyrin HOMO–LUMO gap.

The improved solubility of complex **5** compared with the analogues described[16] allowed us to record its NMR spectra and completely assign their ^{1}H and ^{13}C resonances (see Scheme 2 and Online Supplementary Materials). The distortion of the molecule of dimer **5** revealed by ^{1}H NMR spectroscopy (Figure 2) is apparently caused by the steric hindrance from *meso*-aryl groups located near the connection moiety, which results in the decrease in their rotation rate. In turn, the distorted structure of the molecule results in the non-equivalence of magnetic environment of aromatic *ortho*-protons located on the opposite sides of porphyrin plane. In a similar way, less significant but still noticeable broadening of *ortho*-proton signals has been observed for the aryl groups of other type.

In summary, the presence of the electron-donor substituents at *meso*-positions of the porphyrin core promotes a spontaneous oxidative dimerization of the corresponding nickel(II) 2,3-diaminoporphyrinate. The influence of these substituents on the electronic properties of the obtained dimer is observed as notable bathochromic shift of its absorption bands. The results reported herein extend the scope of panchromatic bridged porphyrin arrays.

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Table 1 Available UV-VIS data of complex **5** and analogous pyrazine-fused porphyrin dimer metal(II) complexes.

Ar	λ_{max}/nm[a]					Reference
4-$BuOC_6H_4$ (**5**)	424sh	491	552	585	622	This work
4-Bu^t-2,6-$Me_2C_6H_2$	420	490	562	586	625	19
2,4,6-$Me_3C_6H_2$	417	488	561	585	623	19
4-MeC_6H_4	417	488	–[b]	583	620	20
3,5-$Bu^t_2C_6H_3$	407	481	533	569	599	16
Ph	402	492	–[b]	–[b]	592	17[c]

[a] λ_{max} are measured in $CHCl_3$ for **5** and in CH_2Cl_2 for the known compounds. [b] The corresponding bands are present in the spectra, but their exact positions were not reported in the original papers. [c] For Zn^{II} complex.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.03.010.

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