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COMMUNICATION

Unexpected formation of the nickel *seco*-tribenzoporphyrazine with a tribenzotetraazachlorin-type absorption spectrum†‡

Victor N. Nemykin,*[a] Anna E. Polshyna,[a] Elena A. Makarova,[ab] Nagao Kobayashi*[c] and Evgeny A. Lukyanets*[b]

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Minor products in the reaction between substituted 1,3-diiminoisoindolines and 2,5-diamino-3,4-dicyanothiophene were identified as the nickel *seco*-tribenzoporphyrazines 4 and 5, which have been characterized by UV-vis, MCD, NMR, and mass spectroscopy. Experimentally observed tetraazachlorin-type UV-vis spectra of new *seco*-tribenzoporphyrazines were explained on the basis of DFT and TDDFT calculations.

Phthalocyanines and their analogues were studied because of their industrial importance as dyes, pigments, and catalysts as well as their ability to mimic biologically relevant electron- and atom-transfer reactions.[1] During the last several decades, however, in addition to the traditional areas of applications, these chemically and thermally robust systems with well-defined photophysical, coordination, and redox properties were intensely investigated as promising photosensitizers for photodynamic therapy of cancer, charge carriers for copiers and printers, redox-driven fluorescence markers and materials for molecular electronics, light-harvesting components in dye sensitized solar cells, and materials for gas sensors.[2] In many cases, such high-tech applications require preparation of the low-symmetry phthalocyanine analogues with the target substituents located at specific positions of the macrocyclic core. As a result of this requirement, many strategies were proposed for synthesis of low-symmetry phthalocyanines and their analogues.[3] *Seco*-porphyrazines represent a rare class of low-symmetry phthalocyanine analogues in which one or several α–β or β–β pyrrolic carbon–carbon bonds are cleaved and transformed into the different functional groups.[4,5] It has been shown that these macrocycles exhibit enhanced optical and fluorescence properties, which make them potential candidates for biomedical applications.

[a] *Department of Chemistry & Biochemistry, University of Minnesota Duluth, Duluth, MN 55812, USA. E-mail: vnemykin@d.umn.edu; Fax: +1 218 726 7394; Tel: +1 218 726 6729*
[b] *Organic Intermediates & Dyes Institute, Moscow 123995, Russia. E-mail: rmeluk@niopik.ru*
[c] *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai, 980-8578, Japan. E-mail: nagaok@m.tohoku.ac.jp*

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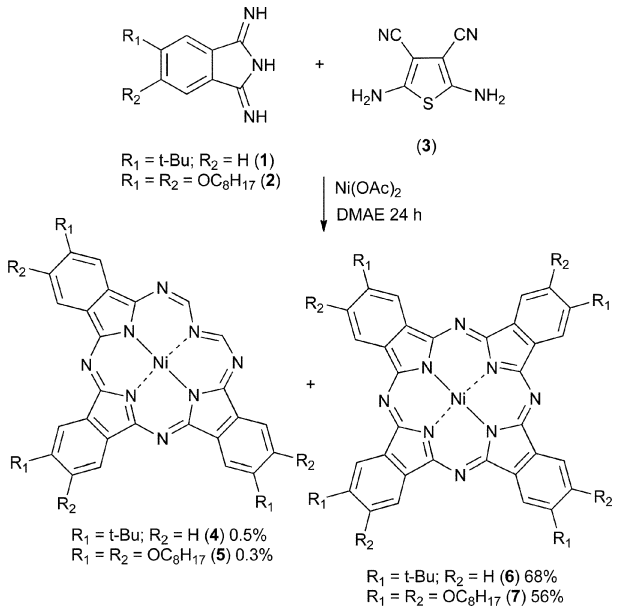
To the best of our knowledge, all of the synthetic strategies reported so far for preparation of *seco*-porphyrazines[4,5] and their close analogues *seco*-porphyrins[6] require oxidative cleavage of the pyrrole ring(s). In this communication, we describe an unexpected formation of the simplest nickel *seco*-tribenzoporphyrazines in the reaction between substituted 1,3-diiminoisoindolines and 2,5-diamino-3,4-dicyanothiophene, which represent an earlier unknown class of *seco*-tribenzoporphyrazines.

In an attempt to prepare functionalized low-symmetry thiophene analogues of nickel phthalocyanine, we have investigated cross-condensation between 5-*tert*-butyl-1,3-diiminoisoindoline **1** and 2,5-diamino-3,4-dicyanothiophene **3** using nickel ions as the template. After 24 h of refluxing the reaction mixture in *N*,*N*-dimethylaminoethanol, however, we were able to isolate only symmetric nickel phthalocyanine **6** (68% yield) as the major reaction product (ESI‡). In addition, during purification workup, we noticed reproducible formation of the very minor (0.5% yield) blue colored reaction by-product, which, based on the spectroscopic and theoretical data presented below, was assigned to the new nickel *seco*-porphyrazine complex **4** (Scheme 1). It should also be noted that no other phthalocyanine-type or expanded phthalocyanine-type[7] compounds were isolated from or identified in the reaction mixture. The formation of complex **4** is very sensitive to the solvent. Indeed, we were not able to isolate any *seco*-porphyrazine products when the reaction was conducted in bromonaphthalene, trichlorobenzene, butanol, or DMF and thus the role of the solvent in the formation of complex **4** remains unclear.

In the absence of X-ray data, the structure of the new *seco*-porphyrazine **4** was established on the basis of spectroscopic and theoretical methods. First, we found that the retention time in size-exclusion experiments for *seco*-porphyrazine **4** was longer compared to that for the symmetric phthalocyanine **6** suggesting a smaller molecular weight for minor product **4**. In agreement with this observation, both FAB and APCI mass spectra of *seco*-porphyrazine **4** are dominated by the peak with $m/z = 665$, which corresponds to the $[M + 1]^+$ ion (ESI‡). In addition, low intensity peaks with $m/z = 682$ and 649, which correspond to the $[M + H_2O]^+$ and $[M - CH_3]^+$ ions were observed in APCI and FAB spectra (ESI‡). Further APCI MS/MS experiments on *seco*-porphyrazine **4** suggested a loss of the peripheral substituents[8] (*i.e.* methyl and *tert*-butyl groups in **4**; ESI‡) that is typical for porphyrinoids. In agreement with the



Scheme 1 Synthesis of *seco*-porphyrazines **4** and **5**.

structure of *seco*-porphyrazine **4**, its ^{1}H NMR spectrum has signals originated from protons in *seco*-fragments of the molecule observed between 9.9 and 10.2 ppm (ESI‡), which are close to the chemical shifts for C–H protons in the earlier reported *seco*-porphyrazines.[5a] The complex pattern observed in the ^{1}H NMR spectrum for *seco*-protons as well as benzene and *tert*-butyl protons is characteristic for the positional isomers expected for *seco*-porphyrazine **4** (ESI‡). It is important to note that the *seco*-protons in **4** are not exchangeable with D_2O thus eliminating any possibility of the presence of –OH or –NH groups in the macrocycle. In order to gain further insight in the spectroscopy of individual isomers of *seco*-porphyrazine **4**, we attempted a separation of the individual isomers using high-performance TLC approaches, which resulted in isolation of one individual isomer of **4** (ESI‡). The ^{1}H NMR spectrum of this isomer is significantly easier to interpret. Indeed, it is indicative of two slightly different *seco*-protons and three different *tert*-butyl groups with two of them being in close chemical environments, which was interpreted as the characteristic pattern for isomer **4a** or **4b** (ESI‡). Because of the well-known[1] negligible influence of the *tert*-butyl group on the absorption spectra of phthalocyanines, it was not surprising to see that the UV-vis spectra of the isomer mixture and individual isomers of *seco*-porphyrazine **4** are virtually the same and consist of intense Q_x and Q_y bands centered at 723 and 593 nm as well as B-band observed at 331 nm (Fig. 1). In addition, a relatively weak band at 412 nm was also observed in the UV-vis spectrum of *seco*-porphyrazine **4**. The MCD spectrum of the *seco*-porphyrazine **4** reflects its low-symmetry nature. Indeed, all of the most intense bands observed in the UV-vis spectrum of **4** (Q_x, Q_y, and B bands) correspond to three intense Faraday *B*-terms, centered at 727, 595, and 338 nm (Fig. 1). The observed negative sign of the low energy Q_x band and positive sign for higher energy Q_y band are characteristic of phthalocyanine-type compounds[9] and indicative of the smaller energy difference between the porphyrazine core-centered LUMO and LUMO + 1 π* MOs (ΔLUMO) than between the porphyrazine core-centered HOMO and HOMO − 1 π MOs (ΔHOMO).[10]

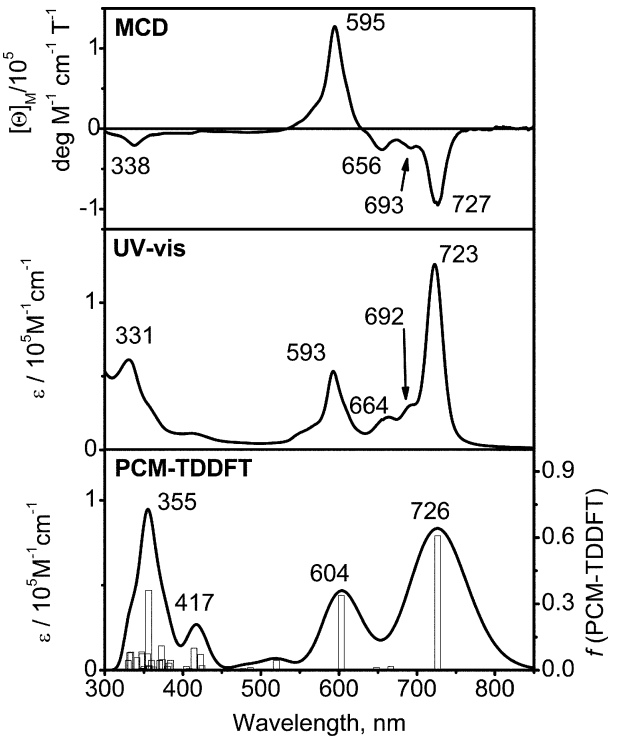


Fig. 1 MCD, UV-Vis, and BP86/6-31G(d) PCM-TDDFT predicted UV-vis spectra of *seco*-porphyrazine **4** in DCM.

It can be speculated that the π-system in new *seco*-porphyrazine **4** resembles the π-system in nickel tribenzotetraazachlorins.[11] Indeed, UV-vis and MCD spectra of *seco*-porphyrazine **4** on the one hand, and nickel tetramethyltribenzotetraazachlorin[11a] or β-oxatetraazachlorins[11b] are very close to each other with respect to the transition energies as well as relative band intensities. In order to clarify the nature of these similarities, we explored the electronic structure and calculated vertical excitation energies in **4** using PCM-DFT and PCM-TDDFT approaches, which are proven to provide reliable electronic structures and spectroscopic signatures in numerous phthalocyanines and their analogues.[12] The PCM-DFT predicted energies and frontier orbitals are shown in Fig. 2, while MO compositions are given in ESI.‡ The HOMO in *seco*-porphyrazine **4** has π-character and resembles an a_{1u}-type (D_{4h} notation) HOMO in transition-metal phthalocyanines. This MO is well-separated (~0.5 eV) from the closely spaced predominantly nickel-centered HOMO − 1 (d_{xz}), HOMO − 2 (d_{z2}), and HOMO − 3 (d_{yz}) with the HOMO − 2 having significant contribution from the *seco*-fragment of the macrocycle. The HOMO − 4 is a mixture of the *n*-orbital localized at *meso* nitrogen atoms and the nickel-centered d_{xy} orbital (Fig. 2). Similar to the other phthalocyanine compounds,[12] this MO has higher energy than the second occupied macrocycle-centered π-orbital (HOMO − 5). PCM-DFT predicts that the virtual, nickel-centered MO is a LUMO + 1, while both LUMO and LUMO + 2 are centered at the *seco*-porphyrazine core. The presence of the nickel-centered MOs in the frontier orbital region should result in numerous transitions with predominant MLCT or LMCT character. Indeed, PCM-TDDFT calculations predict the numerous MLCT and LMCT transitions over the large energy envelop (ESI‡). In general, PCM-TDDFT predicted and experimental data for

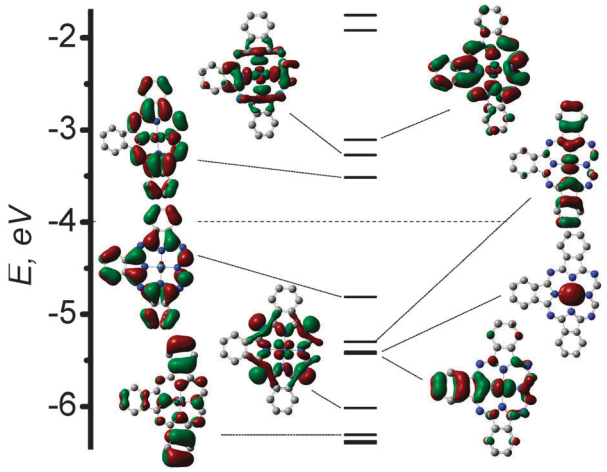


Fig. 2 MO energies of **3** and **4** predicted by DFT calculations. The dashed line designates the HOMO–LUMO frontier.

seco-porphyrazine **4** are in excellent agreement (Fig. 1). Specifically, it is predicted that the Q-band region is dominated by two intense π–π* transitions predominantly originating from the HOMO → LUMO and HOMO → LUMO + 2 excitations. In addition, MLCT and LMCT transitions contribute to the intensities of the higher energy shoulder of the Q_y band at ~600 nm and the low intensity band at ~410 nm. Finally, the most intense transition calculated in the B-band region has predominant π–π* character.

In order to explore the applicability of the new route for the synthesis of the *seco*-porphyrazine core we studied the reaction between **3** and 5,6-bis(octyloxy)-1,3-diiminoisoindoline (Scheme 1). Similar to the previous case, we were able to purify a small amount of *seco*-porphyrazine **5** (0.3% yield), which has UV-vis and MCD spectra that are very close to those of **4** (ESI‡). In addition, the mass and ^{1}H NMR spectra of **5** are in a good agreement with the proposed structure. It could be speculated that the reaction mechanism for the formation of new *seco*-porphyrazines should include cleavage of the C–C bonds in the initial thiophene-substituted low-symmetry phthalocyanine (ESI‡).

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