



Cite this: *Chem. Commun.*, 2023, 59, 3739

Received 6th December 2022,  
Accepted 11th February 2023

DOI: 10.1039/d2cc06648c

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## Oxidative insertion of amines into conjugated macrocycles: transformation of antiaromatic norcorrole into aromatic azacorrole<sup>†</sup>

Sha Li,<sup>a</sup> Yahan Sun,<sup>a</sup> Xiaofang Li,<sup>\*a</sup> Oskar Smaga,<sup>b</sup> Sebastian Koniarz,<sup>b</sup> Miłosz Pawlicki<sup>c</sup> and Piotr J. Chmielewski<sup>b</sup>  

**A new group of aromatic porphyrinoids was obtained by an oxidative insertion of primary amines into the antiaromatic ring of 5,14-dimesityl-norcorrolatnickel(II) activated by iodosobenzene. The substituted 10-azacorroles thus formed were characterized by spectroscopic and electrochemical methods, and XRD analysis. Protonated forms of azacorroles were shown to remain aromatic despite disconnection of the original  $\pi$ -electron delocalization path.**

The aromaticity and antiaromaticity of complex polycyclic systems have attracted the attention of chemists of various fields owing to theoretical interest in these phenomena as well as a potential applicability.<sup>1–17</sup> Porphyrinoids constitute a class of macrocyclic systems that include both aromatic and antiaromatic species.<sup>18–24</sup> The prominent representatives of the planar tetrapyrrolic porphyrinoids, *i.e.* aromatic corrole (**Corr**)<sup>25,26</sup> and antiaromatic norcorrole (**nCorr**)<sup>27–29</sup> both possess twenty  $\pi$ -electron pools but differences in the macrocyclic scaffolds allow  $18\pi\epsilon$  porphyrin-like (**Por**) delocalization in the former and  $16\pi\epsilon$  delocalization in the latter (Fig. 1). An interplay between the aromaticity and antiaromaticity of porphyrinoids involves oxidation/reduction processes<sup>30–35</sup> or alteration of the  $\pi$ -electron delocalization path achieved by the macrocycle skeleton modifications.<sup>19–21,28,31,32,36–50</sup>

Originally reported 10-azacorroles have been obtained by annulation of the predefined linear dipyrin precursors,<sup>37,39,40</sup>

and likewise the *N,N'*-substituted diazaporphyrins and their complexes.<sup>31,32,38,51</sup> We found out that a broad family of *N*-substituted azacorroles can be synthesized in a one-step one-pot reaction of readily obtainable 5,14-dimesitylnorcorrolatnickel(II) **1** with primary amines (Table 1).<sup>52,53</sup> In the present paper, the structural, spectroscopic, redox, and acid–base characteristics of this novel group of porphyrinoids are presented.

In the early stage of our studies, we reacted **1** with aniline, *o*-, *m*-, and *p*-toluidine, or *m*- and *p*-anisidine in the presence of an excess of isoamyl nitrite previously used as a nitrating agent.<sup>30</sup> The reaction gave rise to insertion products, *i.e.*, 10-*N*-(aryl)-5,15-dimesityl-10-azacorrolatnickel(II) with about 30% yield after 30 min of reaction time at room temperature in dichloromethane. No reaction, however, was observed for amines with strongly electron-withdrawing substituents on the amine aryl rings. Thus, we tested several catalysts with rational anticipation that they should act as oxidants generating an active form of the norcorrole. Our survey involved  $\text{FeCl}_3$ ,  $\text{MnO}_2$ ,  $\text{PbO}_2$ ,  $\text{Mn}_2(\text{OAc})_3$ , PIFA ( $\text{PhI}(\text{OCOCF}_3)_2$ ), *m*CPBA,  $\text{PhI}(\text{OAc})_2$ ,  $\text{PhIO}$ , *p*-chloranil, and DDQ, which were applied to the reaction of **1** with 4-chloroaniline. Only for iodosylbenzene, the reaction ran effectively yielding 61% of 10-*N*-(4-chlorophenyl)-5,15-dimesityl-10-azacorrole **3a** (Table 1), and for *p*-chloranil as the oxidant the yield was 8%. A 4.5 times excess of the amine over the norcorrole in the presence of 3.5 equiv. of  $\text{PhIO}$  allowed the highest yield of the azacorrole to be reached. The reaction carried out

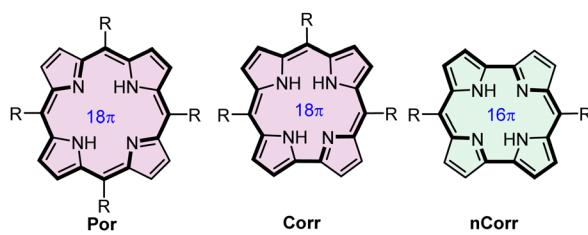


Fig. 1 Schematic representations of the  $\pi$ -electron delocalization paths in selected tetrapyrroles.

<sup>a</sup> Key Laboratory of Theoretical Organic Chemistry and Functional Molecules, Ministry of Education, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology Xiangtan, Hunan 411201, China. E-mail: [liaoxfang@hnu.edu.cn](mailto:liaoxfang@hnu.edu.cn)

<sup>b</sup> Department of Chemistry, University of Wrocław, F. Joliot-Curie 14, Wrocław 50 383, Poland. E-mail: [piotr.chmielewski@chem.uni.wroc.pl](mailto:piotr.chmielewski@chem.uni.wroc.pl)

<sup>c</sup> Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, Kraków 30 387, Poland

<sup>†</sup> Electronic supplementary information (ESI) available: Synthetic and separation details, spectroscopic characterization of the compounds, electrochemistry, and crystallographic data. CCDC 2217087, 2217088, 2217094, and 2217098. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2cc06648c>



Table 1 Synthesis of 10-R-azacorrolatonickel(II)

Entry	Product	R	Time (h)	Yield <sup>a</sup> (%)
1	3a	4-ClPh	2.0	61
2	3b	4-BrPh	2.0	54
3	3c	4-FPh	2.0	65
4	3d	4-NO <sub>2</sub> Ph	1.0	71
5	3e	4-CNPh	1.5	81
6	3f	4-CHOPh	2.5	84
7	3g	4-CO <sub>2</sub> MePh	2.5	72
8	3h	3-ClPh	1.0	80
9	3i	3-BrPh	1.0	82
10	3j	3-FPh	2.5	82
11	3k	3-MePh	2.5	78
12	3l	3-OMePh	2.0	74
13	3m	2,6-Cl <sub>2</sub> Ph	4.0	26
14	3n	2,6-Br <sub>2</sub> Ph	4.0	24
15	3o	4-MePh	4.0	52
16	3p	Ph	4.0	55
17	3q	Et	20	26
18	3r	Pr	7.0	39
19	3s	4-OMePh	12	N.D. <sup>b</sup>

<sup>a</sup> Isolated yields, reaction conditions: **1** (0.052 mmol, 1 equiv.), **2** (0.234 mmol, 4.5 equiv.), PhIO (0.18 mmol, 3.5 equiv.), CH<sub>2</sub>Cl<sub>2</sub> (5 mL), room temperature. <sup>b</sup> The product was obtained with isoamyl nitrite instead of PhIO with 30% yield after 30 min.

under the same conditions for other amines gave rise to azacorrole products with 24–84% yields (Table 1). No azacorrole was formed for *p*-anisidine, *p*-aminophenol, 1,4-diaminobenzene, or 3,4,5-trimethoxyaniline, likely due to oxidation of these amines by PhIO. Significantly, the reaction of **1** with another hypervalent iodine oxidant PIFA has been shown<sup>54</sup> to result in a regioselective macrocyclic ring fission at the bipyrrole  $\alpha$ - $\alpha'$  bond leading in the presence of alcohols to linear tetrapyrroles terminated symmetrically with alkoxy-groups.<sup>54</sup> On the other hand, reactions of **1** with primary amines have been reported to result in mono- or bis-aminated norcorroles.<sup>55</sup> Apparently, a mild oxidant (PhIO) is sufficient to produce a cationic radical [**1**]<sup>•+</sup> that reacts with the amine molecule at the initial step of the reaction.

The new compounds were characterized by high-resolution mass spectrometry, <sup>1</sup>H and <sup>13</sup>C NMR, optical spectroscopy, and for selected systems, also by single crystal X-ray diffraction analyses (Fig. 2 and Tables S6 and S7, ESI<sup>†</sup>).<sup>56</sup> HRMS confirmed the compositions of all azacorrole products, while four doublets of the pyrrole  $\beta$ -protons in the region of  $\delta$  7.2–8.3 ppm in <sup>1</sup>H NMR spectra clearly indicated the effective twofold symmetry of the molecule and aromatic character of these systems. The obvious differences among the spectra of **3a–s** arose from the presence of various substituents at N10. The crystal structures (Fig. 2) revealed the planarity of the macrocyclic rings with a marginal ruffling distortion in **3d**, **3e**, and **3h** and slight

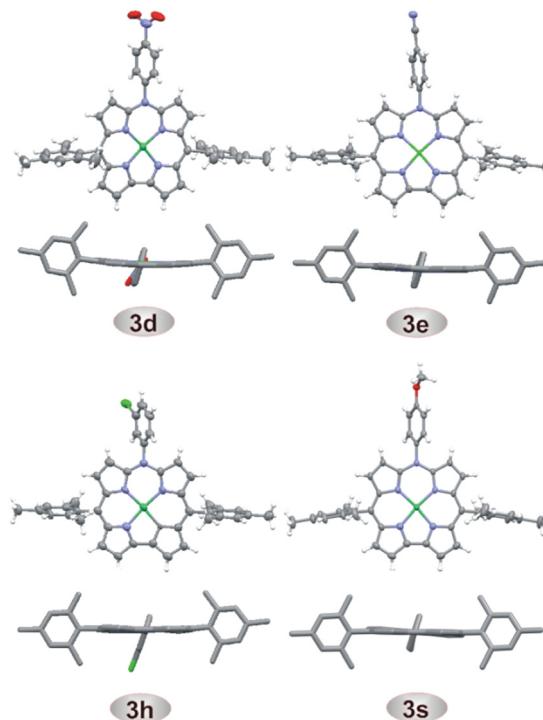


Fig. 2 Thermal ellipsoid (50% probability level, front projections) and stick representations (side views with all hydrogens omitted) of 10-(*p*-NO<sub>2</sub>Ph)-, 10-(*p*-CNPh)-, 10-(*m*-ClPh)-, and 10-(*p*-OMePh)-5,15-dimesityl-10-azacorrole nickel(II) complexes.

saddling distortion in **3s** (Fig. S114–S117, ESI<sup>†</sup>).<sup>57</sup> The absorption spectra of all the systems were similar with a Soret-like band at 395 nm and three weaker Q-bands at 563–565 nm, 586–592 nm and 630–643 nm. These spectra were also similar to that of unsubstituted or *N*-acetylated azacorroles<sup>37</sup> and strongly differed from that of the parent norcorrolatonickel(II) **1** reflecting a change from antiaromaticity of **1** to aromaticity of the azacorrole ring. The cyclic voltammetry (Fig. S118–S136 and Table S1, ESI<sup>†</sup>) showed two reversible oxidation processes (ox1, ox2) for all the systems with potentials  $E_{\text{ox1}}$  ranging from 0.13 to 0.22 V and  $E_{\text{ox2}}$  from 0.67 to 0.75 V (all potentials vs. Fc/Fc<sup>+</sup> internal standard). Apparently, the oxidations occurred at potentials similar to those reported for the parent system **1**. The potentials of reversible first reductions  $E_{\text{red1}}$  (from –2.15 to –2.05 V) were similar to those observed previously for other 10-azacorrolatonickel(II) complexes<sup>37</sup> but about 1.1 V lower than the first reduction potential of **1**.<sup>28,30</sup> The TD DFT calculated HOMO–LUMO energy gap (2.21 eV for **3d**) was close to the difference between the first oxidation and first reduction potentials ( $e(E_{\text{ox1}} - E_{\text{red1}}) = 2.36$  eV for **3d**, Table S1, ESI<sup>†</sup>). Thin-layer spectroelectrochemical measurements in DCM indicated a ligand-centered oxidation (Fig. S144 in ESI<sup>†</sup>) with a significant decrease of the Soret-like band intensity, hypsochromic shift of this band (from 396 to 360 nm) as well as broadening and bathochromic shift in the Q-band region (to 667 and 702 nm). These changes indicated loss of the aromatic character of the macrocycle in **3p**<sup>•+</sup> upon removal of the first



electron<sup>58–61</sup> likely due to involvement of the *meso*-nitrogen electron lone pair in the delocalization path of **3**. Chemical oxidation of **3p** with tris(4-bromophenyl)ammonium hexachloroantimonate (BAHA, Magic Blue)<sup>62,63</sup> resulted in similar spectral changes (Fig. S145 and S146 in ESI†). A BAHA-generated EPR spectrum of **3p**•<sup>+</sup> confirmed the radical character of the mono-oxidized species<sup>64–67</sup> with an isotropic signal at  $g_0 = 2.0198$  (RT, DCM, Fig. S147, ESI†) and frozen-solution spectrum of orthorhombic symmetry and small anisotropy of the Zeeman tensor ( $g_1 = 2.0295$ ,  $g_2 = 2.0193$ ,  $g_3 = 2.0042$ , see Fig. S149 in ESI†) at 77 K.<sup>47,60,64–67</sup>

Addition of trifluoroacetic acid (TFA) to a solution of **3** in  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  resulted in reversible spectral changes (Fig. 3A and Fig. S140–S142, ESI†). The full conversion into the protonated form required high excesses of the acid, *i.e.* 2–5% (v/v) of TFA. These changes can be fully reversed by the addition of the equivalent amount of triethylamine. The protonation was also monitored by low-temperature  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 220 K) to slow down chemical exchange. Addition of 1% of TFA resulted in the appearance of a new set of sharp signals attributed to the protonated species  $[\mathbf{3iH}]^+$  (Fig. 3B). The 2D homo- and heteronuclear NMR experiments indicated pyrrole  $\beta$ -carbon C3 as an exclusive protonation site (Fig. 3B and Fig. S150–S154, ESI†) despite the apparent lack of any steric factors discriminating among the four distinct targets.

However, deuteration by means of TFA-*d* ( $\text{CDCl}_3$ , 220 K) revealed that all pyrrole  $\beta$ -CH's, except equivalent sites at C7 and C13 were subjected to the isotope exchange (Fig. S155 in ESI†). The DFT-determined relative stability of  $[\mathbf{3dH}]^+$  tautomers unequivocally indicated C3/17 as the most, while C7/C13 as the least favorable protonation sites among pyrrole  $\beta$ -carbons, in line with the experimental results (Fig. 3C and Table S17, ESI†). The  $\text{sp}^3$  hybridization of C3 revealed by its chemical shift in the  $^{13}\text{C}$  NMR spectrum ( $\delta_{\text{C}} 48.1$  ppm) indicated disconnection of the original  $\pi$ -electron conjugation path at the protonated pyrrole. Despite that, the macrocyclic aromaticity of azacorrole in the protonated state was retained as it could be inferred from chemical shifts of the pyrrole  $\beta$ -protons in an aromatic region of  $\delta$  7.2–7.7 ppm (Fig. 3B). The GIAO-calculated proton chemical shifts for  $[\mathbf{3dH}]^+$ , negative sign of all NICS(1) values determined over the centroids of each ring, and anisotropy of the induced current density (AICD) were in line with the aromaticity of 3-protonated azacorrolatnickel(II) (Fig. 3D). To account for this, canonical structures with positive charge localized at the pyrrole  $\beta$ -carbon adjacent to the protonation site, thus allowing  $18\pi$ -electron conjugation, are needed to be involved in the resonance (Fig. 3D).

In conclusion, a series of nickel(II) complexes of *N*-substituted 10-azacorroles were obtained using oxidative insertion of primary amines into oxidant-activated antiaromatic norcorrolatnickel(II).

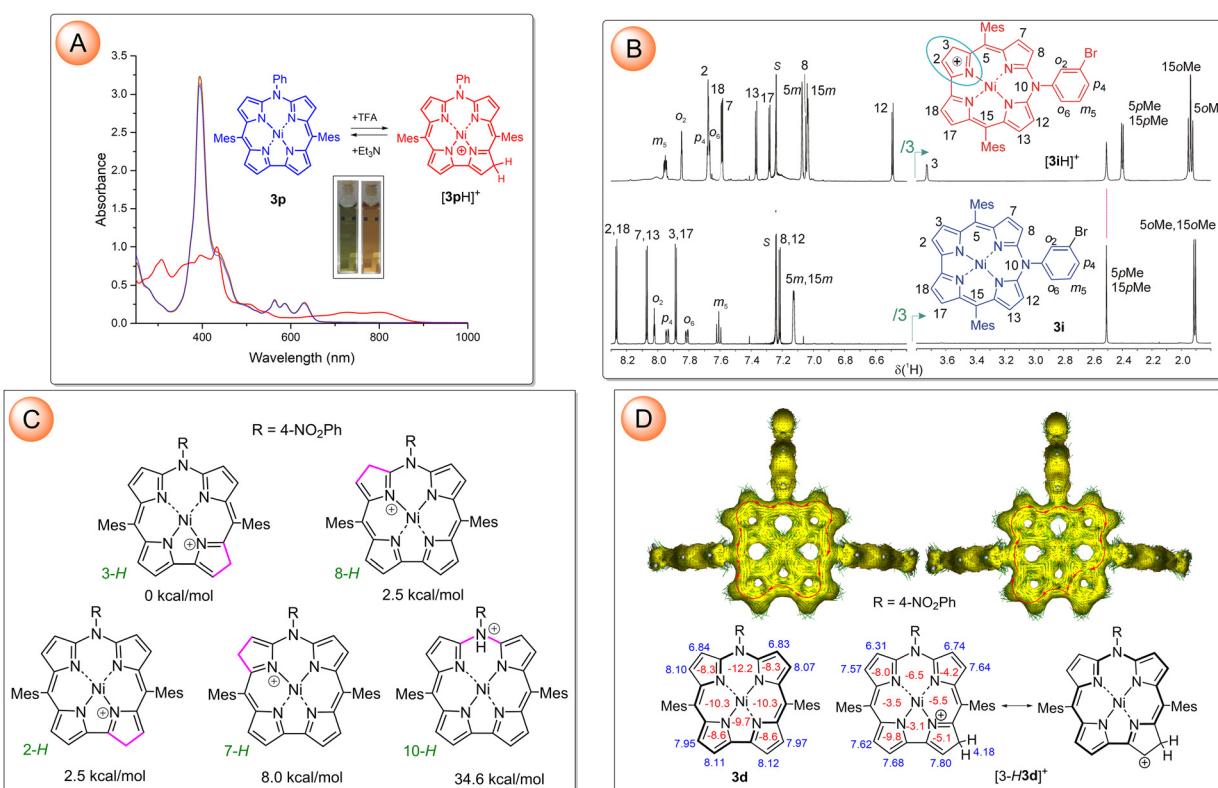


Fig. 3 (A) Superimposed UV-vis-NIR spectra of the **3p** solution in DCM (brown trace), that was recorded upon addition of TFA (10 equiv., red trace), and after neutralization with  $\text{Et}_3\text{N}$  (10 equiv., blue trace). (B) Expansions of selected regions of  $^1\text{H}$  NMR spectra of **3i** (lower trace) and its protonated derivative  $[\mathbf{3iH}]^+$  (upper trace) with the signal assignments ( $\text{CDCl}_3$ , 220 K). Note that in the high-field region, the intensities of the signals are divided by the factor of 3. (C) Structures of possible tautomers of  $[\mathbf{3dH}]^+$  with relative energies of the DFT-optimized models. (D) GIAO-calculated chemical shifts (blue numbers), NICS(1) indices (red numbers), and AICD plots (0.03 isosurface) calculated for **3d** (left column) and  $[\mathbf{3-H3d}]^+$  (right column).



The compounds obtained in this way were diamagnetic, aromatic, and electron-donating. Despite neutral character and the lack of an obvious protonation site, nickel(II) azacorroles appeared to be proton acceptors. Macrocycles protonated at one of the pyrrole  $\beta$ -carbons remained aromatic. The electron donating properties of the azacorrolatonicel(II) are reflected also by relatively low oxidation potentials allowing facile generation of the radical species. Further study on these compounds will involve exploration of their potential in organic electronic devices.

This work was supported by the National Natural Science Foundation of China (No. 22171076), the Science and Technology Innovation Program of Hunan Province (2021RC5028), and the Polish National Science Center (2018/29/B/ST5/00280). Quantum chemical calculations were performed in the Wrocław Centers for Networking and Supercomputing. Publication of this article was supported by the Excellence Initiative – Research University program for the University of Wrocław.

## Conflicts of interest

There are no conflicts to declare.

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