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Synthesis and electron-transport property of stable antiaromatic Ni^{II} norcorrole with the smallest *meso*-substituent

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meso-Dimethylnorcorrole Ni^{II} complex exhibited enough stability under ambient conditions despite the distinct antiaromaticity. The small methyl substituents realized a dense and long-range π stacking in its solid state, which resulted in the superior electrontransporting ability to previously reported Ni^{II} norcorroles.

Stability is a basic, yet the essential physical property of organic molecules. In particular, π -conjugated molecules with high stability are attractive because they not only enable the comprehensive studies on their fundamental properties relating to conjugation, charge transfer and photophysical process, but also allow the fabrication of practical devices with high durability. The Hückel rule predicts that cyclic π -systems with 4n+2 π -electrons gain substantial stability, so-called aromaticity.¹ They have been indispensable components of various practical materials such as plastics, medicines, dyes and (opto)electronic devices.²

Planar cyclic π -systems with 4n π -electrons display antiaromaticity.^{3,4} Antiaromatic molecules are unstable. Indeed, several antiaromatic molecules exhibit higher reactivities toward both electrophiles and nucleophiles rather than aromatic molecules.⁵ Consequently, the current molecular designs of antiaromatic compounds are invariably associated with thermodynamic and kinetic stabilization.⁶ However, thermodynamic stabilization strongly perturbs the electronic structures of the π -systems, which diminishes their intrinsic properties such as narrow HOMO-LUMO gap and multi-redox capabilities. Kinetic stabilization by sterically hindered peripheral substituents prevents effective intermolecular interactions in the condensed phases. This situation is not suitable for the fabrication of solid-state materials such as organic rechargeable batteries7 and ambipolar semiconductors.⁸ In this regard, a stable antiaromatic molecule with a small peripheral substituent should be a fascinating research target.



Fig. 1 Structures of β -octaethylnorcorrole 1, dimeric norcorrole 2 and *meso*-substituted norcorroles 3–7.

Norcorrole is a ring-contracted porphyrinoid, which lacks two meso carbons from a regular porphyrin (Fig. 1).9-11 Norcorrole contains 16 π -electrons in its macrocyclic conjugation, thus being antiaromatic. In 2008, the synthesis of β-octaethylnorcorrole Fe^{III} complex **1** was accomplished by Bröring and co-workers.⁹ Unfortunately, **1** was not isolable because the rapid dimerization of 1 afforded the corresponding dinorcorrole 2. In contrast, meso-dimesityInorcorrole Ni^{II} complex **3** was stable under ambient conditions.¹⁰ These results revealed that the bulky mesityl groups kinetically stabilize the inherently reactive meso-positions of norcorroles. Nevertheless, our recent studies demonstrated that smaller peripheral substituents such as phenyl and isopropyl groups are sufficient to yield bench-stable derivatives 4 and 5.11 We also detected the generation of Ni^{II} meso-dihexylnorcorrole 6 by NMR analysis.^{11c} However, **6** was not isolated in a pure form due to the presence of inseparable impurities. The smallest substituent to stabilize the antiaromatic norcorrole core has remained unclear.

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Electronic Supplementary Information (ESI) available: experimental details and spectral data for all new compounds. Crystallographic data (CIF files) for **7**. See DOI: 10.1039/x0xx00000x

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In this work, we investigated the stability of *meso*substituted norcorrole Ni^{II} complexes toward air, water, heat and silica-gel. Furthermore, we accomplished the synthesis and isolation of Ni^{II} *meso*-dimethylnorcorrole **7**, which is a stable Ni^{II} norcorrole with the smallest *meso*-substituent. Interestingly, **7** exhibited the superior electron-transporting ability due to its dense molecular packing in the solid state.



Scheme 1 Synthesis of meso-dimethylnorcorrole 7.

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Because Ni^{II} norcorroles exhibit the distinct antiaromaticity, they are essentially unstable and reactive. The current research started with a comparison of the stability of Ni^{II} mesodimesityInorcorrole **3** and Ni^{II} meso-diphenyInorcorrole **4** upon the exposure to air, water, silica-gel and heat. The solid samples of 3 and 4 were stored for 2-4 months under ambient conditions, resulting in no detectable degradation (Fig. S8-S11, ESI). The stability of **3** and **4** in solution was also examined by monitoring their ${}^1\!H$ NMR spectra in CDCl_3 after the storage under ambient conditions for 1 week. This experiment again confirmed no detectable spectral change (Fig. S12, S13; Table S2, ESI). Norcorroles 3 and 4 were also robust to conventional purification such as washing with water and silica-gel chromatography (Fig. S14-S17, ESI). Solutions of 3 and 4 in toluene were heated at 80 °C under air for 16 h but these molecules were recovered in almost quantitative yields (Fig. S18, S19, ESI). These results indicate that relatively small phenyl groups are enough to stabilize the antiaromatic norcorrole core, enabling the treatment under ambient conditions with no special care. During this study, we noticed that 4 displayed 2-10 times lower solubility in comparison to 3 (Table S1, ESI). Then, we established an improved procedure without purification by silica-gel chromatography, which afforded 4 in a good yield of 56% (Scheme S1, ESI).^{11a}

These studies encouraged us to quest for the smallest substituent to stabilize the antiaromatic norcorrole core. We set Ni^{II} *meso*-dimethylnorcorrole **7** as the target molecule because *meso*-unsubstituted norcorrole **1** was too reactive to be isolated as a stable molecule. Bromination of 5-methyldipyrromethane **8** with *N*-bromosuccinimide (NBS) followed by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) afforded dipyrromethene **9**, which was unstable under aerobic conditions. The reaction mixture was subjected to metalation

with Ni(OAc)₂·4H₂O without purification to provide the corresponding dipyrrin Ni^{II} complex **10** Provide 112% Feb Photometer steps. Reductive coupling of **10** provided Ni^{II} meso-dimethylnorcorrole **7** in 24% yield. Norcorrole **7** showed low solubility in various solvents (0.2 g/L in CH₂Cl₂).

Importantly, Ni^{II} meso-dimethylnorcorrole **7** was sufficiently stable under ambient conditions on the contrary to our anticipation. The storage of the solid samples under ambient conditions for at least one month resulted in no detectable decomposition (Fig. S22, ESI). In addition, a solution of 7 in CH₂Cl₂ was monitored by the absorption spectra, suggesting that 7 underwent negligible degradation (ca. 3.4%) after 24 h under ambient conditions (Fig. S20, ESI). According to this result, we estimate the half-life time of 7 in a CH₂Cl₂ solution to be about two weeks. Furthermore, Nill mesodimethylnorcorrole 7 was robust to silica-gel chromatography and required no special treatment during the work-up process. It is worth noting that the apparent degradation was observed after heating the toluene solution at 80 °C, in which ca. 50% of 7 underwent decomposition after 12 h (Fig. S21, ESI). Since none of the meso-unsubstituted norcorroles have been isolated to date, the methyl group is the smallest substituent to stabilize the antiaromatic norcorrole core.







Fig. 4 UV/Vis/NIR absorption spectra of 3 (black), 4 (green), 5 (blue) and 7 (red) in CH_2CI_2 . λ = wavelength.

Fig. 3a displays the ¹H NMR spectrum of Ni^{II} mesodimethylnorcorrole **7** in CDCl₃. The signals due to θ -protons appeared at 3.11 and 2.42 ppm, which were upfield-shifted from those of normal pyrroles (ca. 6–7 ppm). In addition, the signal due to the *meso*-methyl protons was observed at –0.96 ppm. The calculated NICS(1) values¹² are in the range of 2.8– 31.2 ppm (Fig. 3b and Fig. S29, ESI). These results suggest the Published on 25 September 2020. Downloaded by Auckland University of Technology on 10/5/2020 7:50:49 AM

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presence of a distinct paratropic ring current. The UV/Vis/near-IR(NIR) absorption spectrum of **7** in CH_2Cl_2 shows peaks at 422, 472 and 505 nm as well as a weak absorption band tailing to the NIR region (Fig. 4). This spectral feature resembles those of other norcorrole derivatives. These results indicate the negligible perturbation of the methyl groups on the electronic structure, especially the antiaromaticity, of the norcorrole core.

Fig. 5 X-ray crystal structure of *meso*-dimethylnorcorrole **7**. (a) Single-molecule structure and (b) packing structure. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

Fig. 5 shows the crystal structure of Ni^{II} mesodimethylnorcorrole 7. In the crystal, 7 exhibits almost planar structure with the mean planer deviation (MPD)¹³ of 0.01 Å, which is comparable to those of other norcorroles 3 and 5 (0.03–0.04 Å). The harmonic oscillator model of aromaticity (HOMA) value¹⁴ is 0.32, which is also comparable to those of other norcorroles 3 and 5 (0.43–0.46). These results suggest the negligible perturbation by the methyl groups on the structure of the norcorrole core. In the crystal of 7, one-dimensional columnar π -stacking with an interplanar distance of 3.31 Å is observed (Fig. 5b). The short contact between two norcorrole core in **7** is striking because π - π stacking distances typically range from 3.4 to 3.6 Å. On the other hand, each norcorrole unit of 3 is separated due to bulky mesityl groups (Fig. S25, ESI). Diisopropylnorcorrole **5** also shows no effective overlap of π systems (Fig. S27, ESI). Diphenylnorcorrole 4 adopts a tripledecker stacking structure with a short π - π distance of 3.15 Å. However, the stacked trimer does not form continuous π staking (Fig. S26, ESI). Consequently, dense and long-range π stacking is only observed in the crystal of 7.

Norcorrole exhibits a deep-lying LUMO level due to its antiaromaticity.¹⁵ The one-dimensional columnar alignment in a slipped parallel manner of **7** inspired us the stacking axes as potential and stable electron-conducting pathways. Indeed, our calculations predicted that the π -stacking afforded a large

intermolecular charge transfer integral of 64 meV_{ic}(Fig.c6a)_{nll} p contrast, the calculated transfer integrals in 9 and 9 were tess than 14.2 meV (Fig. S30, ESI). Ni^{ll} meso-diphenylnorcorrole **4** showed a large transfer integral (130.9 meV) between two stacking macrocycles. However, the transfer integrals between neighbouring triple stacks were small (<27.3 meV), suggesting the lack of an effective electron-conducting pathway in **4**.



Fig. 6 (a) Effective transfer integrals (meV) of LUMO calculated for the nearest intralayer neighbours in the crystal structure of **7**. (b) Photoconductivity transients recorded in microcrystalline **3** (blue), **4** (orange), **5** (violet) and **7** (red), respectively upon excitation at 355 nm, $0.2-1.3 \times 10^{15}$ photons cm⁻², RT.

We examined the electronic photo-conduction of 3, 4, 5 and 7 by flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurement in their microcrystalline states.¹⁶ Electrodeless photocarrier injection was performed upon excitation at 355 nm where the electronic transitions of the series of molecules are minimum, securing the homogeneous photocarrier distribution in their crystalline states. The observed photoconductivity transients were shown in Fig. 6b. Dimethylnorcorrole 7 marked the highest photoconductivity over all time regime up to ~100 µs. Kinetic trace of 7 exhibits clearly double exponential decay with the first-order rate constants of 4 \times 10⁶ and ~10⁴ s⁻¹. To assess the major contribution from photo-generated electrons and holes onto the columnar stacking of 7, the effects of O_2 on conductivity transients were observed as shown in Fig. S28. Conductivity signals were significantly suppressed and quenched by O₂ particularly for the initial decay in the transients, which is suggestive of the major contribution of electrons in photoconductivity as presumed by the LUMO levels of norcorrole cores. It should be noted that quenching by O_2 was indistinct for the longer decay component in conductivity

transients. This may be due to the conductivity transients observed at >1 μ s reflected mainly by the local motion of electrons within μ m-sized crystallites of 7, followed by surface quenching by O₂. One order of magnitude higher photoconductivity was recorded for 7 in contrast to negligible change in conductivity of 3, 4 and 5. This is the case of impacts by the methyl substitution onto the dense crystalline structure and hence onto the stable electronic conducting pathways.

In summary, we investigated the stability of several norcorrole Ni^{II} complexes toward the exposure to air, water, silica-gel and heat. Furthermore, we achieved the synthesis of Ni^{II} *meso*-dimethylnorcorrole **7**, which was considerably stable under ambient conditions despite its distinct antiaromaticity. Currently, the methyl group is the smallest substituent to afford a stable norcorrole Ni^{II} complex. Importantly, **7** exhibited the superior electron-transporting ability to other Ni^{II} norcorroles owing to its dense and long-range π -stacking. The current research should offer new insight into the design of stable antiaromatic molecules with small peripheral substituents.

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Conflicts of interest

There are no conflicts to declare.

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TOC



A stable and antiaromatic norcorrole Ni^{II} complex has been synthesized with a small substituent, which exhibited good electron-transporting ability.