

Meso-1,4-phenylene bridged nickel norcorrole dimer

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Dedicated to Professor Atsuhiro Osuka on the occasion of his 65th birthday.

Received 28 May 2019 Accepted 23 July 2019

> **ABSTRACT:** Nickel norcorrole dimer **3** linked with a phenylene bridge was prepared by a nickelmediated homolytic cross-coupling of *meso*-phenylene bisdipyrrin nickel(II) dimer **2b**. The structures of **2b** and **3** were elucidated by X-ray diffraction analysis. Each nickel norcorrole fraction of the nickel norcorrole dimer **3** exposed a bowl-like structure, which conserved anti-conformation. Structural distinctions between the monomeric and dimeric nickel norcorroles were established by vibrational spectroscopic analysis and assessed with density functional theory calculations. Enhanced flexibility of the norcorrole planes in solution states of monomeric nickel norcorrole was compromised to that of bowl-shaped norcorroles in the solid states of nickel norcorrole dimer **3**, where C_{2v} was the formulated conformation. The deformation of the planarity derived from the objection of laser pulses effectuated vibration shifts of specific Raman-active motions toward a higher-frequency region, as associating with a paratropic nature of the π -electron delocalization circuit of norcorrole. Computational simulation exposed a reliable drift of the Raman frequencies.

> **KEYWORDS:** norcorrole, nickel complex, crystal structure, dimer, antiaromaticity, vibration spectroscopy.

INTRODUCTION

Conformational distortion of the π -conjugated system has had an increase in interest due to the dynamics of their electronic configurations [1]. Porphyrins that exhibit 18 π -electron conjugation networks stabilize the electronic configurations by the delocalization of π electrons [2]. Vibrations of the porphyrin skeletons arising from artificial bulky substituents such as saddling, waving, and twisting have been induced with spectroscopic methods [3–7]. Notably, captivations deliberated from their powerful aromatic features, various metal coordination capabilities as well as their abundance in nature are all aspects that have inspired the various biochemical/ biotechnological investigations [8, 9].

Nickel norcorrole (NiNC) has been introduced as a unusually stable antiaromatic molecule exhibiting a 16π -electron conjugation, whose stabilization was enhanced by the metal coordination. Norcorrole first was introduced in a DFT analysis by Ghosh and coworkers in 2005 [10] and a further-stabilized dimerization of norcorrole was reported in his recent research [11]. The first isolation and spectroscopic characterization of norcorrole was succeeded with Fe(III) norcorrole by Bröring et al. in 2008 [12]. Shinokubo and coworkers have reported an efficient gram-scale synthetic method of NiNC, which also promoted further investigations [13-16]. The main skeleton of norcorrole exhibited conformational dependencies upon the chelated metals due to its smaller cavity compared to the cores of typical porphyrins [16]. A highly planar structure of mesityl NiNC was elucidated by X-ray diffraction analysis [13]. Cu(II) norcorrole exposed a higher planarity than both free-base and Pd(II) norcorroles, in which significant sets of resolved signals were detected in hyperfine and superhyperfine couplings of single unpaired electrons with Cu (I = 3/2) and four Ns (I = 1/2) nuclei, respectively due to the small norcorrole cavity. Furthermore, the palladium norcorrole exhibited a substantial level of antiaromaticity

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and a bowl shape. NiNC has shown common antiaromatic behaviors and proficiency for practical applications such as active electrode materials in organic batteries [17, 18].

NiNC has been developed to dimeric NiNCs. In 2015, Chmielewski and coworkers reported that hydrogenation of NiNC in the presence of Raney nickel produced a highly hydrogenated species, and advanced oxidation of the species with *p*-chloranil yielded a heterodimerized NiNC molecule [19]. Homodimerized NiNC molecules have also been introduced in recent research by Shinokubo and coworkers [20]. However, NiNCs that were linked by meso-arylene were not reported. A convenient synthetic method of NiNC dimers having simple 1,4-phenylene linkers was accomplished as shown in Scheme 1. Herein, we prepared a novel NiNC dimer 3 having a 1,4-phenylene linker whose molecular structure was elucidated by X-ray diffraction analysis (Scheme 1). The unique antiaromatic behaviors of NiNC are still detected with the NiNC dimer 3. Furthermore, an enhanced/upright implementation of interacting waves of two NiNC fractions was investigated in comparison with the spectroscopic performance of the monomeric NiNC origin. Spectral analysis and computational calculation were also investigated for the confirmation of coherence between the actual analysis and the theoretical calculation.

RESULTS AND DISCUSSION

The precursor 2b was prepared in a similar method to that earlier reported in the literature (Scheme 1) [21]. Tetradentate nickel complex dimer 2b was then conducted to the nickel-mediated homo coupling to produce the target, nickel norcorrole dimer 3 (Scheme 1). Tetradentate nickel complexes have responded distinctly to external magnetic fields in accordance with distorted angles of the coordination ligands. Dipyrrins are monoanionic and bidentate ligands that form neutral complexes with numerous metal ions and have shown self-assembling



Scheme 1. Nickel-mediated reductive coupling of dipyrrin nickel complex dimer 2b toward *meso*-phenylene NiNC dimer 3



Scheme 2. Preparation method of the precursor 2b for the *meso*-phenylene bridged NiNC nickel complex dimer 3

features through metal coordination. Tetrahedral nickel complexes exhibit paramagnetic properties due to the two unpaired *d*-orbital electrons of the nickel center, whose hyperfine (electron-nuclear) couplings enlarge the range of the magnetic field. The degree of the dihedral angles between two nickel-chelated dipyrrin-planes plays an essential role in associating the magnetic distinction [21–23]. The steric factor on external α positions of pyrroles is, therefore, the key controlling the distorted angles as well as the magnetic behaviors of nickel complexes. Metal coordination of dipyrrin dimers often resulted in high degree polymerizations [24]. On the other hand, such cascades are inhibited by interruptions of monomeric dipyrrins, which become the terminating blocks of polymers. α, α' -dibromodipyrrin dimer 1 was associated with the nickel complexation of meso-mesityl- α, α' -dibromodipyrrin, which acts as a controller of the metallation degree (Scheme 2). Modifications to the synthetic method somewhat improved the yield of the target product 2b. However, the result of the reaction was still a mixture of the products, 2a-2d, having a different degrees of Ni-metallations. Precursor 2b was then conducted to the nickel-mediated homo coupling to form the nickel norcorrole dimer 3 (Scheme 1).

Single crystals of **2b** were grown in an CH_2Cl_2 solution by a vapor diffusion of *n*-hexane (Fig. 1) [25]. Alignments of the molecular units revealed a channel in the unit lattices. Hexane solvent molecules were disordered to fill the space of channels and located close to each other (Fig. S1). The growth of single crystals of **2c** was also accomplished successfully in the same solvent system chosen for **2b** (Fig. 2) [26]. No solvent molecule was



Fig. 1. Crystal structures of the *bis*dipyrrin Ni(II) complex dimer 2b: Thermal ellipsoids are scaled at the 50% probability level



Fig. 2. Crystal structure of the bisdipyrrin Ni(II) complex trimer 2c: Thermal ellipsoids are scaled at the 50% probability level

found in the crystal lattice. Loss of the linearity of the overall structure as the degree of metallation increased was significant.

Moreover, very few single crystals of hemi-molecule of **2c** were obtained in the same sample for the crystal growth of **2c** [27]. The crystal shape and color of hemi-molecule of **2c** were precisely distinguishable with those of **2c** crystals. Since only a few crystals of the hemi-molecule were found, it was presumed that the demetallation of the central nickel happened in a tiny amount during a long-term process of the single-crystallization.

Preparation of 3 was successful in nickel mediated cross coupling of the precursor 2b by using the consistent method of NiNC [13] and it was improved by the use of 2,2'-bipyridine and Ni(cod)₂ to a *ca*. 30% yield. The growth of single crystals of 3 was successful in a reversible vapor diffusion of methanol and chloroform. The molecular structure of the NiNC dimer was then elucidated by the crystallographic method [28]. No solvent molecule was found in the unit lattice. The structure of dimeric NiNC projected an immense distinction to the structure of monomeric NiNC, in which the main norcorrole planes bulged in opposite vectoring axial directions from the nickel centers. As a result, the overall dimeric structure presented waved planes, exposing a particular interaction between the two NiNC segments. As shown in Fig. 3, the structure of 3 showed a curved plane for each unit, which resulted in a shortened

distance from one side terminal mesityl to the other terminal mesityl (approximately, 0.7 Å was shortened). The packing diagram of the crystal is presented in Fig. 4, in which intermolecular stacking was observed in each half-molecular shifted position. The distance between the terminal mesityl carbons in **2b** was 30.891 Å while the distance in the crystal data of NiNC dimer **3** was 30.126 Å. The solubility of **3** in particular organic solvents was drastically reduced after the crystallization. The well-aligned packing was perhaps a critical reason for the reduced solubility.

All dipyrrin nickel complexes **2a–2d** exhibited extended ranges of chemical shifts (-5.1–60 ppm) in the respective ¹H NMR spectra (Fig. S5). On the other hand, the ¹H NMR spectrum of the norcorrole dimer **3** presented its proton peaks in a range typical of chemical shifts for diamagnetic Ni complexes. The spectral data awarded symmetric configuration of the two reflecting NiNC units centering the 1,4-phenylene bridge, in which a paratropic ring current of antiaromatic norcorrole was observed (Fig. S6). Four doublets at 2.00, 1.52, 1.49, and 1.41 ppm were assigned as the peaks of β Hs of norcorrole. HH COSY NMR (Fig. S7) exposed two respective correlations for the sets of the doublets.

As shown in Fig. 5, the overall pattern of absorption bands for 3 overlapped mostly with the absorption bands of NiNC monomer. Those were somewhat broadened and extended over 1100 nm. The broad absorptions express



Fig. 3. Crystal structure of 3: (a) top view and (b) side view. Thermal ellipsoids are scaled at the 50% probability level



Fig. 4. Packing diagram of NiNC dimer 3: (a) top view and (b) side view. Thermal ellipsoids are scaled at the 50% probability level



Fig. 5. Absorption spectra of 3 and NiNC monomer in CH₂Cl₂

precise interactions between the NiNC units through the covalently linked phenylene. The forbidden S_0 - S_1 transition was buried in an extended wavelength area in the monomeric NiNC, which was appreciated with the intermolecular interaction. The molecular arrangement observed in a crystalline state (Fig. 4) could be a frozen conformation. Intermolecular interactions would be enhanced with the enlarged molecular surfaces in the NiNC dimer. The TD-DFT calculation data was in high agreement with the measured absorptions (Fig. 6). As the concentration of **3** increases in CH_2Cl_2 solutions, the absorbance of the absorption band, appearing at the long wavelength area, was enhanced. Furthermore, the absorption band up to 1100 nm was retained in the absorption spectra, even with a very diluted CH_2Cl_2 solution of **3**.

The cyclic voltammogram of 3 shown in Fig. 7 was associated with a 1.0 V/s scan rate. The cyclic voltammogram of 3 proposed stepwise oxidation of four electrons and stepwise reduction of four electrons. A split of the first oxidation potential was observed. It is hypothesized that an imbalanced two-electron oxidation

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Fig. 6. TD-DFT spectra of **3** in CH_2Cl_2 : (a) measured and (b) calculated (TD-DFT/B3LYP/SDD) spectra

proceeded. Once both NiNC segments were oxidized, with one electron each, a second oxidation happened identically with a reversible redox potential. However, the first reduction involving two electrons happened equally and reversibly and the second reductions were imbalanced (Fig. S11). When the measurement was speed up (0.05 V/s to 0.1 V/s), the second reduction potentials became irreversible, and further speeding up broadened and flurried the reduction potentials, which were eventually undetectable. The HOMO–LUMO gap of **3** (the difference of the first oxidation and first reduction potentials) was slightly smaller than that of NiNC monomer (0.92 V and 1.08 V for **3** and NiNC, respectively).

Vibration spectroscopic experiments were attempted in order to rationalize the structural dynamics. Measurements of the vibration bands were accompanied with single crystals of the corresponding molecules. Figure 8 shows the FT-IR spectra of the precursors of NiNC monomer and NiNC dimer **3** and the NiNC molecules in solid states. Those crystalline states of monomeric NiNC and dimeric **3** resulted in characteristically distinct vibration bands (Figs 8c and 8d) in the FT-IR spectra (Fig. 8), as judging from the partial alternation in between those structures. Some single vibration bands that appeared in Fig. 8c were found as two separated vibration bands in Fig. 8d. For example, a symmetric and in-plane scissoring vibration was split into two vibration bands due to the different symmetric center (nickel for NiNC and 1,4-phenylene for the NiNC dimer 3). Out-of-plane vibration of meso-aryls at 748 cm⁻¹, with motion aligning in the same direction were split into two vibrations, one for the external meso-mesityls and the other for 1,4-phenylene. This is due to the better planarity of norcorrole than of the bisdipyrrin Ni(II) complex. Three *meso*-aryls of **2b** are largely distorted. The dihedral angles increased among the aryl planes compared to the angles for the mesoaryls of 3. Two vibration bands of 3 are found at 739 and 743 cm⁻¹ (Fig. S22). On the other hand, bisdipyrrin nickel complexes 2a and 2b disclosed an identical pattern of IR-responded vibration bands between monomer and dimer (spectra a and b) in the FT-IR spectra, as judging from the sum of the vibrations of two independent monomeric metal complexes. Changes of the vibration energies were understood to be a bumped-up orientation of the nickel center of NiNC in 3, where out-of-plane vibrations were created. A different composition of the dipole moments at the two metal coordination sites gave rise to the change of vibration energies and appearance of new vibration bands.

Resonance Raman spectroscopy resulted in resembled Raman-active bands for a CH₂Cl₂ solution of NiNC and a crystalline sample of **3**. On the other hand, both CH_2Cl_2 solution and crystalline state of NiNC contributed the reliable vibration sequences in the Raman spectra (spectra a and c in Fig. S14). The strong correlation between structural distortions of nickel porphyrins and their consequent vibration bands was reported by Dietsek and coworkers [29]. Core-size marker lines are one of the most significant sequences for the recognition of the structural relationship of either the molecular core sizes or Ni–N distances and the vibration frequencies of the group. The associated results were reported with tetrapyrrole-containing, Ni-chelated proteins, whose vibrations have been observed in $\sim 1300-1500 \text{ cm}^{-1}$ [30]: Fingerprint regions were considered to account for the types of *oop* (out-of-plane) distortions. The distortion momentum commenced shifts of the structural sensitive ip (in-plane) modes to lower frequencies. Compared with porphyrins, norcorrole has a condensed core size whose complexes bear high repulsions between the electrons filled in *d*-orbitals of nickel and the ligation electrons donated from four Ns of norcorrole. Raman resonance sequences of the high planar NiNC whose structure was



Fig. 7. Cyclic voltammograms of 3 in CH_2Cl_2 (0.1 MnBu₄NPF₆). Working electrode: glassy carbon, counter electrode: Pt, reference cell: Ag/AgCl₄, and Fc/Fc⁺: ferrocene/ferrocenium couple



Fig. 8. FT-IR spectra of (a) **2a**, (b) **2b**, (c) NiNC monomer, and (d) **3**, measured in respective neat solid states and zoomed in at a range of 400–2000 cm⁻¹

supported by crystallographic results gave an opposite observation to nickel porphyrin. Ni(II) is suitable to fit in the core of norcorrole due to the reduced size of the core in the absence of two *meso*-methines, which provide a planar structure with a minimum N-Ni distance. The N-Ni distance increases with the formation of bowl-shaped NiNC because of the bump-up orientation of the metal center from the norcorrole plane. On the other hand, a large core in porphyrin with the small radius Ni(II) distorts the planarity and reduces the N-Ni distance. Ni-N distance is maximized in the enhanced planarity of Ni(II) porphyrin. For porphyrins, due to the existence of four methine groups, the contribution of dom (A_{2n}) deformation (Dom is consistent with a bowl shape in this paper and, considering the citation [16]), is relatively smaller than others in the symmetric normal-coordinate deformations: sad (B_{2u}), ruf (B_{1u}), wav (E_{gx}), wav (E_{gy}), and pro (A_{1u}) [31]. However, the norcorrole macrocycle desired to gross the orientation, dom-deformation, which was retained in the X-ray structure of 3, suggesting the main symmetric deformation. Another substantial difference of norcorrole from porphyrin is the paratropic ring current of π -electron density delocalization [14–16]. The distinct magnetism was also hypothesized to switch the normal behaviors of frequency shifts on the distortion motion. Entire vibration frequencies of NiNC in respective solution and solid (single crystals were used for the spectroscopic study) states, measured with the first-time radiations in 532 nm, were virtually identical. An improved planar C_{2h} structure was estimated with the NiNC monomer in both the initial solution and solid states, as supported by its crystal structure reported earlier [13]. Further Raman spectroscopy of the NiNC samples with correspondingly extended time intervals of resonance irradiations provided different sequences of Raman spectra.

A CH_2Cl_2 solution sample of NiNC gave rise to executed band disappearances and band shifts in 2nd-time excitations using a 532 nm laser pulse



Fig. 9. Low Frequency region of the 532 nm excited Resonance Raman spectra of NiNC monomer in CH_2Cl_2 solution: (a) 1st time and (b) 2nd time laser excitations (5 scans with 15 s irradiation interval)



Fig. 10. 532 nm excited Resonance Raman spectra of NiNC monomer in CH_2Cl_2 solution: (a) 1st time and (b) 2nd time laser excitations (5 scans with 15 s irradiation interval)

(Figs 9 and 10). As shown in Fig. 9, the oop-mode frequency appeared around 262 cm⁻¹ (spectrum a) shifted to 282 cm⁻¹ (spectrum b), performing an opposite directional shift of typical aromatic porphyrins. Calculated Raman-active oop-mode frequencies were obtained at 164 and 169 cm⁻¹ for the planar and bowllike structures of NiNC, respectively (Fig. S24 a and b). Furthermore, ip scissoring vibrations of NiNC, which associate with the symmetric plane, dividing two dipyrrin groups, shifted from 434 cm⁻¹ (planar) to 440 cm⁻¹ (bowlshaped). There was no significant Raman active frequency at 200–300 cm⁻¹ obtained from the calculated vibrations. Two *ip* rocking vibrations (1481 and 1490 cm⁻¹) of planar NiNC were calculated to take a closer location (1481 and 1486 cm⁻¹) in bowl-shaped NiNC (Fig. S24, spectra c and d). The two separated bands appeared to become a broadened single band as shown in Fig. 10. The similar aspect was seen around 870 cm⁻¹, in high aggreement with the calculated vibrations (Fig. S24, spectra e and f). A single vibration band found at 686 cm⁻¹ was observed by the first excitation. By the second excitation, an additional weak vibration band appeared at 650 cm⁻¹ with a vibration band at 692 cm⁻¹. The measured Raman frequencies were consistent with the calculated Raman frequencies, supporting the conformation change from the planar structure to the bowl-shaped structure for NiNC. The influences appeared to suggest the increase of Ni–N distances and enhancement of planarity, based on Raman projection of porphyrin. Dynamic processes on the double-dipole model of ring current effects have been investigated to improve the deformation of planarity of porphyrin plane and π -electron delocalized aromatic system in nuclear magnetic resonances. Those dynamics that were deliberated on antiaromatic norcorroles influenced an opposite chemical shift. It was assured that the results of Raman motions were reflected with the paratropic sequence of overall electron-spin vectors. The degree of flexibility in a solution state enabled the consequent dynamics. Accordingly, the enhanced ring distortion resulted in the vibration shifts toward a low frequency. Still, no subsequent changes of vibration bands were observed with a crystalline sample of NiNC (Fig. S14, spectrum d). Two frequencies appeared around 1433 and 1485 cm⁻¹ at spectrum a in Fig. 10 shifted to a higher frequency region, 1468 and 1565 cm⁻¹ at spectrum b in Fig. 10, respectively. These results complemented those presented in the literature [29, 30]. Furthermore, it was found that the vibrations shown in the spectrum of NiNC excitation state in a solution corresponded greatly with the spectral vibrations of dimeric NiNC 3 in a crystal (spectra b and c in Fig. S15). Crystals of 3 were also subjected to the Raman spectroscopy with extended time intervals of resonance irradiation, where no changes were observed (Fig. S16). Consequently, the solution state of the NiNC monomer in the excited state was concluded to adopt a consistent conformation with the crystal structure of 3, with the distortion of the planarity. Based on the crystal structure of 3, a bowl-shaped conformation on each skeleton of NiNC cycles of 3 was then considered to be a reliable conformation with the monomeric NiNC. Structurally flexible NiNC molecules in a solution are forced to take lower symmetric conformations when photon energies are introduced to the NiNC molecules.

EXPERIMENTAL

General

All the reagents from commercial suppliers were used without further purification. Chromatographic separations were carried out by silica gel column chromatography (Silica gel 300) and gel permeation chromatography. NMR data of the compounds were measured with Bruker Avance 300 and 500 MHz NMR spectrometers in a CDCl₃ solvent, with the use of an internal standard of TMS. The standard Bruker software was used for homonuclear 1D and homonuclear as well as heteronuclear 2D experiments. X-ray diffractions of the

single crystal of the compound **2** were collected at 141 K, with a Varimax Saturn N instrument and operated using the Rigaku operation software package. The structure was solved using direct methods with SHELXS97 and refined using SHELXL97. All hydrogen atoms were placed in the calculated positions, respectively.

Computation methods

TD-DFT calculation for the optical property of 3was set with the B3LYP basis parameters and a CH_2Cl_2 solvent system. Structure parameters of crystal data, found in the Crystallographic Information File (CIF), were initially used for structure optimization with the symmetric factors. The Gaussian 09 software package performed DFT calculations with a basis set of B3LYP, and the existence of a local minimum was verified for vibration frequency calculation modes. The initial point group symmetries of the bowl and planar NiNCs were set to C_{2v} and C_{2h} , respectively, to constrain the structures for further computations. The wave-shaped structure of **3** was set with the point group of symmetric parameters. C_i was chosen and carried on the further calculation of the vibration frequencies. For comparison, vibrational frequencies were calculated in parallel, without any operating parameter of the symmetric point-group.

Preparation of compound 3

A Schlenk tube containing 100 mg (61 µmol) of 2b and 47.63 mg (305 µmol) of 2,2'-bipyridine was moved into a glove box and 83.9 mg (305 µmol) of Ni(cod)₂ was added into the tube. The resulting solution was stirred for 1 h at 35 °C after the tube was sealed completely. 3 was isolated by the column chromatography on alumina using a mixed eluent of CH₂Cl₂ and hexane. A dark yellow fraction of 3 was separated after a trace amount of pale yellow fraction, oxacorrole which was generated by the oxidation of 3. Glossy crystals of 3 were obtained by a recrystallization from CH₂Cl₂/MeOH Yield 20 mg (33%), Spectral data of 3: HRMS (MALDI-TOF): m/z992.1858 (calcd. for $[M = C_{60}H_{42}N_8Ni_2]^+$ 992.2213) ¹H NMR (300 MHz; CDCl₃: Me₄Si; 25 °C) TMH, ppm 6.195 (4H, s, mesity-H), 5.119 (4H, s, Ph), 2.848 (12H, s, mesity-CH₃), 1.771 (6H, s, mesity-CH₃), 1.362 (4H, d, J = 4.2, pyrrole-*H*), 1.263 (4H, d, J = 3.9, pyrrole-*H*), 1.250 (4H, d, J = 3.9, pyrrole-H), 1.208 (4H, d, J = 4.2, pyrrole-H); TMC NMR (125.8 MHz; CDCl₃; Me₄Si; 26.1 °C) δ_c, 148.2, 147.6, 133.2, 130.7, 129.5, 128.1, 127.1, 128.0, 127.8, 127.7, 119.3, 114.63. 25.6, 17.33.

CONCLUSION

Nickel norcorrole (NiNC) dimer **3**, linked with a phenylene bridge, was prepared by nickel-mediated homo-coupling of *meso*-phenylene bisdipyrrin nickel(II) dimer **2b**. The result of the X-ray diffraction analysis

revealed a uniquely mobilized conformation from the core planarity of monomeric NiNC. The individual norcorrole site of the norcorrole dimer **3** showed a bowl-like (A_{2u}) conformation where the convex and concave sites were switched between each of the two norcorroles. As a result, the overall structure (C_i structure) conserved an letter-S-like conformation. The chemical properties of dimer **3** were established with optical and vibrational spectroscopic analysis and assessed with the TD-DFT calculation data. Enhanced flexibility in solution states of the monomeric NiNC was highly compromised to solid states of bowl-shaped NiNC dimer **3**. The formulated conformation is also in good agreement with the DFT calculation result.

Nevertheless, the crystal structure of the NiNC monomer took a D_{2h} (E_g) conformation in which high planarity of the NiNC skeleton was exhibited. It differed significantly from the excited solution state of the precursor monomeric NiNC and the crystalline state of dimeric **3**. On the other hand, Raman resonance of the solution states of NiNC exhibited relatively identical sequences of the vibration momenta with the norcorrole dimer **3**. Investigation of various extended NiNC systems and their chemical/magnetic properties are proceeding in our further norcorrole research.

Acknowledgments

Grant-in-Aid for Scientific Research supported this research from NEXT (Japan). We also acknowledge the G30 program foundation of Nagoya University for the support of this work. J-Y. Shin acknowledges Prof. Hiroshi Shinokubo at the Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University for his support. Also, J-Y. Shin thanks Mr. Ryota Ashikaga and Prof. Atsushi Satsuma at the Department of Materials Chemistry, Graduate School of Engineering, Nagoya University Nagoya for Raman spectroscopy.

Supporting information

Crystal structures, NMR spectra, HRMS spectra, cyclic voltammograms, Raman spectra and computation data (Figs S1–S24 and Table S1) are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/ jpp/jpp.shtml. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under numbers CCDC-1876767 (**2b**), CCDC-1877278 (**2c**), CCDC-1877028 (hemi-molecule of **2c**) and CCDC 1845468 (**3**). Copies can be obtained on request, free of charge, *via* http://www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

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- 25. Crystal data of **2b** (CCDC1876767): $C_{60}H_{42}N_8Br_8Ni_2$ (C_6H_{14}) $M_r = 1717.88$, T = 93 (2) K, Crystal size = 0.10 × 0.10 × 0.02 mm³, Mo radiation, triclinic, space group *P*-1 (#2), *a* = 7.847 (2) Å, *b* = 11.996 (4) Å, *c* = 19.330 (6) Å, $\alpha =$ 94.573 (7)°, $\beta = 97.154$ (7)°, $\gamma = 91.271$ (5)°, V = 1798.7 (9) Å³, Z = 1, $P_{calcd.} = 1.586$ g/cm, $R_1(F) = 0.0643$ (I > 2 $\sigma(l)$), $wR_2(F^2) = 0.1757$ (all), GoF = 1.075.
- 26. Crystal data of **2c** (CCDC1877278): $C_{84}H_{54}N_{12}Br_{12}Ni_3$ $M_r = 2366.44, T = 93$ K, Crystal size = $0.08 \times 0.05 \times 0.01$ mm³, Mo radiation, triclinic, space group *P*-1 (#2), a = 13.6554 (4) Å, b = 17.2256 (5) Å, c = 18.9596 (6) Å, $\alpha = 88.008$ (3)°, $\beta = 72.754$ (3)°, $\gamma = 79.889$ (3)°, V = 4192.4 (2) Å³, Z = 2, $P_{calcd} = 1.875$ g/cm, $R_1(F) = 0.0515$ ($I > 2\sigma(I)$), $wR_2(F^2) = 0.1427$ (all), GoF = 1.014.
- 27. Crystal data of hemi-molecule of **2c** (CCDC1877028): $C_{42}H_{28}N_6Br_6Ni_1 M_r = 1154.87, T = 93$ K, Crystal

size = $0.098 \times 0.068 \times 0.002$ mm³, Mo radiation, orthorhombic, space group *Pbca* (#61), (#2), *a* = 9.3075 (1) Å, *b* = 19.1142 (4) Å, *c* = 46.6877 (8) Å, $\alpha = \beta = \gamma = 90^{\circ}$, *V* = 8306.0 (2) Å³, *Z* = 8, *P*_{calcd} = 1.847 g/cm, *R*₁(*F*) = 0.0484 (*I* > $2\sigma(l)$), *wR*₂(*F*²) = 0.1228 (all), GoF = 1.156. 9

- 28. Crystal data of **3** (CCDC 1845468): $C_{60}H_{42}N_8Ni_2$, $M_r = 992.43$, T = 141 K, Crystal size = 0.074 × 0.04 × 0.01 mm³, Mo radiation, triclinic, space group P-1 (#2), a = 9.2609 (11) Å, b = 11.1338 (16) Å, c = 12.279 (2) Å, $\alpha = 86.131$ (7)°, $\beta = 76.463$ (7)°, $\gamma = 66.489$ (5)°, V = 1128.2 (3) Å³, Z = 1, $P_{calcd} =$ 1.461 g/cm, $R_1(F) = 0.0717$ ($I > 2\sigma(I)$), $wR_2(F^2) =$ 0.1717 (all), GoF = 1.067.
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