

Self-Assembly

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A Supramolecular Polymer Constituted of Antiaromatic Ni^{II} Norcorroles

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Abstract: For the creation of next-generation organic electronic materials, the integration of π -systems has recently become a central theme. Such functional materials can be assembled by supramolecular polymerization when aromatic π -systems are used as monomers, and the properties of the resulting supramolecular polymer strongly depend on the electronic structure of the monomers. Here, we demonstrate the construction of a supramolecular polymer consisting of an antiaromatic π -system as the monomer. An amide-functionalized Ni^{II} norcorrole derivative formed a one-dimensional supramolecular polymer through π - π stacking and hydrogen-bonding interactions, ensuring the persistency of the conducting pathway against thermal perturbation, which results in higher charge mobility along the tightly bound linear aggregates than that of the aromatic analogue composed of Zn^{II} porphyrins.

Introduction

Polymers, which consist of repeating structures linked by covalent bonds, have been successfully applied to a wide

range of functional materials due to their high durability, light weight, and processability. On the other hand, the very same high durability can also result in unsustainable materials with high environmental impact.

In recent decades, chemists exploring supramolecular polymerization have been inspired by the dynamic interactions of biological systems such as DNA^[1] and organelles,^[2] which form large periodic structures. Supramolecular polymerization allows the reversible construction of large periodic structures by combining dynamic intermolecular interactions, i.e., hydrogen bonds,^[3] coordination bonds,^[4] or π - π stacking.^[5,6c]

As the function of a supramolecular polymer depends on the properties of its monomer units,^[6] an expansion of the diversity in monomers available for supramolecular polymerization should represent a desirable research target. One attractive class of monomers is π -conjugated molecules, because their delocalized π -electrons can enable higher-order functions such as charge transport,^[7] magnetism,^[8] and energy storage.^[9] However, the use of “aromatic” π -conjugated molecules has been regarded as indispensable in the design of electronic functional supramolecular systems, which are often composed of polycyclic aromatic hydrocarbons, perylene bisimides, or porphyrins.^[10]

In recent years, antiaromatic compounds have attracted considerable attention due to their unique properties,^[11] which include high conductivity,^[12] biradical character,^[13] and multi-redox behavior.^[14] In this context, we became interested in supramolecular polymers that consist of antiaromatic molecules. However, supramolecular polymers based on antiaromatic monomer units have not been reported to date.^[15] The reason for this is the inherent unstable nature of antiaromatic molecules. The common strategy for stabilizing antiaromatic molecules is the introduction of bulky peripheral substituents,^[16] which hampers effective intermolecular interactions between monomers to form self-assembled polymers.

We have recently discovered that Ni^{II} *meso*-diphenyl-norcorrole **1** (Figure 1) exhibits high stability toward air, water, and heat despite its lack of steric protection by bulky *meso*-substituents.^[17,18a] Furthermore, we have reported that the Ni^{II} norcorrole units adopt close π - π stacking with interplanar distances of 3.05–3.26 Å in norcorrole cyclophanes, leading to effective orbital interactions.^[18] If such an effective overlap of π -orbitals of norcorrole macrocycles could be achieved in a long-distance periodic manner, highly efficient charge transport within the molecular assembly could potentially be accomplished. Against this background,

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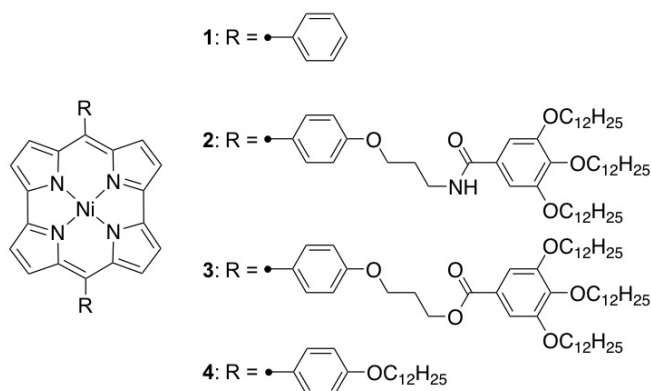


Figure 1. Structures of the *meso*-substituted norcorroles **1–4** used in this study.

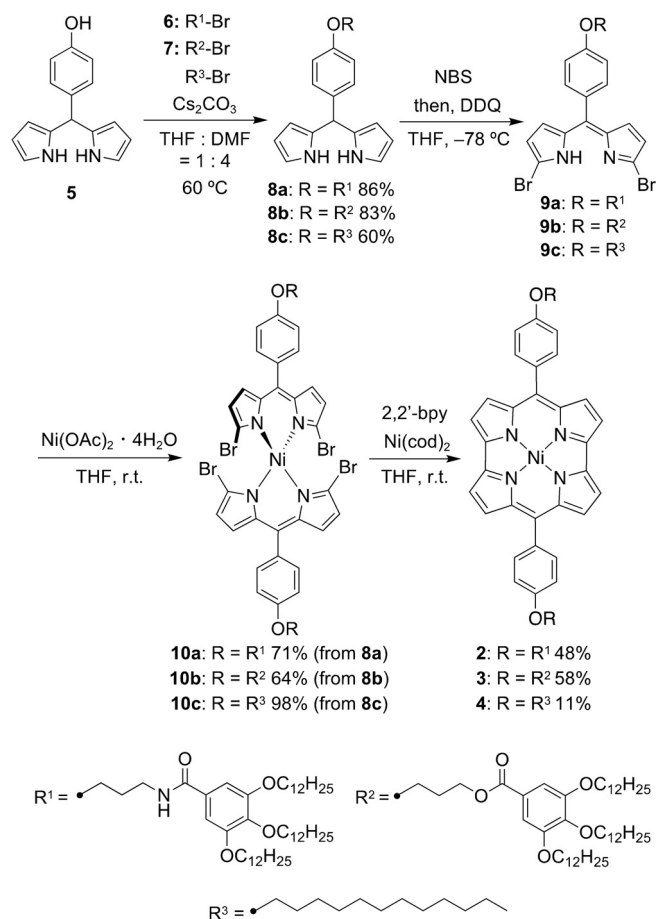
we wanted to explore the supramolecular polymerization of an antiaromatic norcorrole Ni^{II} complex via π -stacking.

Results and Discussion

Inspired by hitherto reported supramolecules that consist of aromatic π -components, we designed norcorrole Ni^{II} complex **2** with amide moieties as hydrogen-bonding sites and long alkyl chains.^[5b,20] Norcorrole **2** is expected to self-assemble via π - π stacking and hydrogen-bonding of the amide groups. Compound **3** and **4** was designed for the aggregation of π -systems via van der Waals interactions among long alkyl chains.

The synthetic route to **2**, **3**, and **4** is illustrated in Scheme 1. Treatment of 5-(4-hydroxyphenyl)dipyrrromethane **5** with long-chain alkyl bromides afforded **8a**, **8b**, and **8c**. Bromination of **8a**, **8b**, and **8c** with *N*-bromosuccinimide (NBS) followed by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) afforded dipyrromethenes **9a**, **9b**, and **9c**. Then, the reaction mixtures were subjected to metalation with Ni(OAc)₂·4H₂O without purification. The reaction provided the corresponding dipyrryn Ni^{II} complexes **10a**, **10b**, and **10c** in three steps in 71%, 64% and 98% yields, respectively. Reductive coupling of **10a**, **10b**, and **10c** provided Ni^{II} norcorroles **2**, **3**, and **4** in 48%, 58%, and 11% yields, respectively. These norcorroles were characterized using NMR spectroscopy and high-resolution mass spectrometry. Fortunately, a single crystal of **3** was obtained by slow evaporation of a chloroform solution, enabling an unambiguous elucidation of its solid-state structure via X-ray diffraction analysis (Figure S34).

Norcorrole Ni^{II} complexes with *meso*-4-alkoxyphenyl groups have not yet been reported. Consequently, we evaluated the electronic modulation of the 4-alkoxyphenyl groups on the antiaromaticity of **2**, **3**, and **4** using ¹H NMR spectral analysis and DFT calculations. In the ¹H NMR spectra of **2**, **3**, and **4** in CDCl₃, the signals of the pyrrole protons appeared in the region δ = 2.06–2.52 ppm (Figures S11, S13, and S15), which is considerably upfield-shifted compared to those of normal pyrroles (δ $\approx$ 6–7 ppm). These chemical shift values are almost identical to those of Ni^{II}



Scheme 1. Synthesis of norcorrole Ni^{II} complexes **2**, **3**, and **4**.

meso-diphenylnorcorrole **1**, which corroborates the presence of a distinct paratropic ring current effect.^[18a] NICS(1) values calculated at the GIAO-BHLYP/6-31G(d) + SDD level ranged from 23.6 to 27.7 ppm except at the pyrrole subunits, which also support the presence of paratropicity of **3** (Table S1).^[21,22]

The electronic modulation was further evaluated using UV-Vis-NIR absorption spectroscopy. The UV-Vis-NIR absorption spectra of **1–4** in CH₂Cl₂ are shown in Figure 2, and all exhibit broad and weak absorption bands tailing to 900 nm. This absorption feature is characteristic for Ni^{II} norcorrole

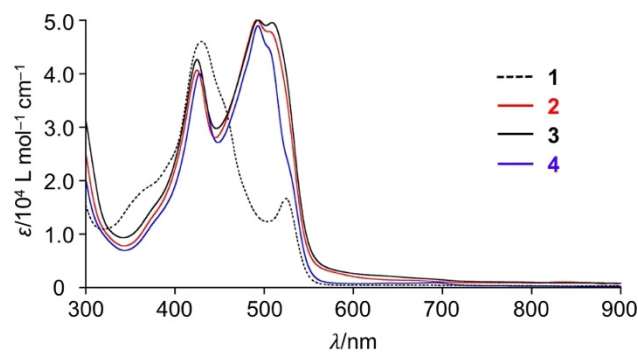


Figure 2. UV-Vis-NIR absorption spectra of **1** (dashed line), **2** (red), **3** (black), and **4** (blue) in CH₂Cl₂; λ = wavelength.

complexes. TD-DFT calculations at the B3LYP/6-31G(d) + SDD level of theory suggest that the weak absorption bands originate from the forbidden HOMO→LUMO and HOMO−1→LUMO transitions (Figure S35 and Table S5). These spectroscopic results and DFT calculations confirm the antiaromatic nature of the norcorrole cores of **2**, **3**, and **4**. The absorption spectra of **2**, **3**, and **4** are similar to each other but differ from that of **1** around 500 nm. This is due to the substituent effect of the 4-alkoxyphenyl groups, which was supported by TD-DFT calculations (Figure S36).

The self-assembly behavior of Ni^{II} *meso*-di(4-alkoxyphenyl)norcorrole **2** was investigated using temperature-dependent UV-Vis-NIR absorption spectroscopy. Upon cooling a hot solution of **2** in cyclohexane/benzene (9/1) from 343 K to 283 K, distinct absorption changes were observed at 423 nm and 484 nm (Figure 3a). A slow cooling rate of 1 K min^{−1} was applied to ensure that the self-assembly process occurred under thermodynamic control.^[19] In fact, the heating and cooling rates were varied from 0.5 to 2.0 K min^{−1}, but no hysteresis curves were observed (Figure S40). The self-assembly and disassembly processes of **2** were monitored via the changes in the absorption band at 484 nm as a function of temperature (Figure 3b). The cooling and re-heating processes were essentially reversible. Because the observed curves seem to be sigmoidal, we first attempted to analyze the association behavior on the basis of the isodesmic model (Figure S44).^[19] However, the experimental curves were not reproduced by the model. Then, the aggregation behavior was

analyzed using the nucleation-elongation model to result in the better curve fit for the observed data (Figure S42).^[23,24] The analysis of the aggregation parameters afforded a molecular enthalpy release of −94 kJ mol^{−1} ([**2**] = 10 μM) (Table S8). Lowering the concentration of **2** resulted in a decrease in the elongation temperature, T_e , but the enthalpy values were almost independent of the concentrations. Plotting the natural logarithm of the concentration as a function of the reciprocal of T_e (van't Hoff plot) yielded the changes in enthalpy and entropy of −96 kJ mol^{−1} and −203 J mol^{−1} K^{−1}, respectively, which is in good agreement with the values derived from modeling the melting curves (Figure S43). In addition, the association behavior of the corresponding ester derivative **3** was investigated under the same conditions as those for **2**. Ester **3** exhibited no association behavior, thus confirming the importance of the amide groups in **2** to undergo self-assembling behavior (Figure S48).

We investigated the morphology of the self-assembled Ni^{II} *meso*-di(4-alkoxyphenyl)norcorrole **2** formed after the cooling process. Transmission electron microscopy (TEM) observations of self-assembled **2** revealed the formation of bundled fibers (Figure 4a). Atomic force microscopy (AFM) afforded topological and phase images of films spin-coated from cyclohexane/benzene (9/1), elucidating the presence of many bundled fibers (Figure 4b). The height profile along the white line in Figure 4b is shown in Figure 4c. The inset of Figure 4c depicts the model structure of **2** obtained from DFT calculations at the B3LYP/6-31G(d) + SDD level of theory.

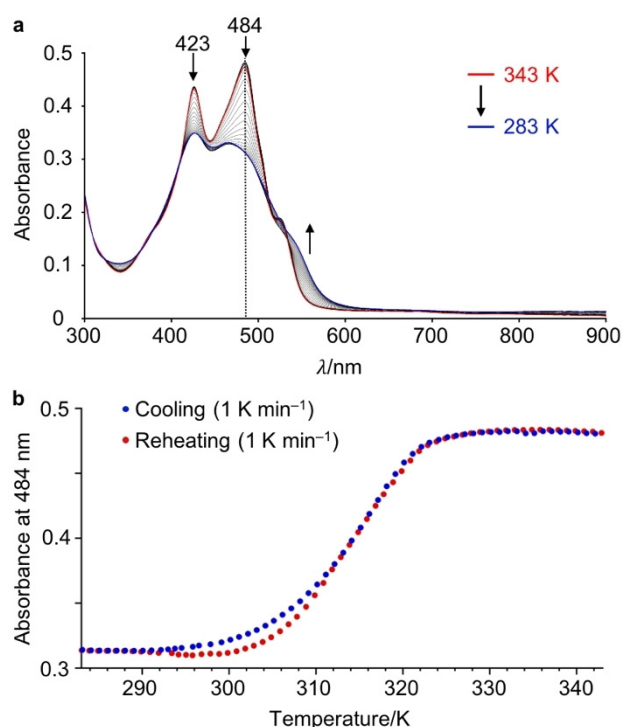


Figure 3. a) UV-Vis-NIR absorption changes of **2** observed during the cooling process in cyclohexane/benzene (9/1) ([**2**] = 10 μM). b) Changes in the absorption at 484 nm as a function of temperature during the cooling and reheating processes.

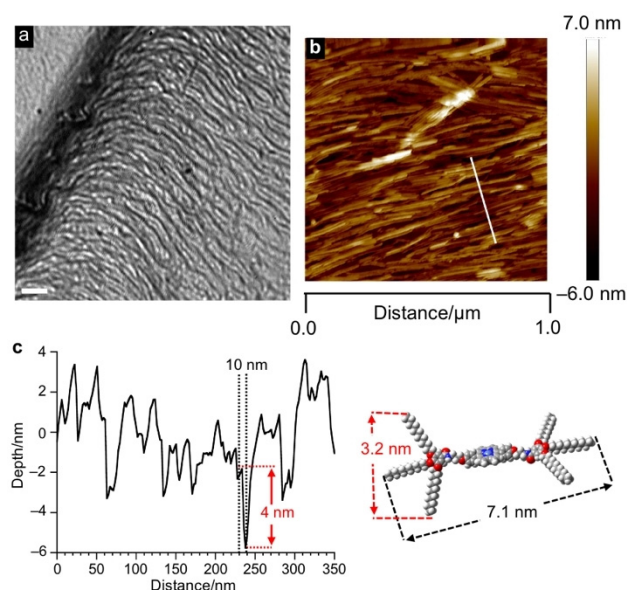


Figure 4. Morphology of self-assembled **2**. a) TEM image of self-assembled **2**. The TEM grid was dipped in a cyclohexane/benzene (9/1) solution of **2** (10 μM) after cooling and dried at room temperature under reduced pressure. The bar is 0.5 μm. b) AFM topological image of a film spin-coated from a diluted solution of **2** in cyclohexane/benzene (9/1) ([**2**] = 10 μM) onto silicon. c) Height profile of the fibers measured along the white line in the AFM image; inset: Simulated structure of **2**; atom color code: Purple, Ni; grey, C; red, O; blue, N; white, H.

The width (10 nm) and height (4 nm) of the peaks shown in Figure 4c are in good agreement with the model diameter (7.1 nm) and the short axis length (3.2 nm). These measurements indicate that **2** forms one-dimensional supramolecular polymers along the π -stacking axis.

We then conducted Fourier-transform infrared (FT-IR) spectroscopy measurements to evaluate the presence of hydrogen-bonding interactions. FT-IR measurements showed that the N-H stretching band of self-assembled **2** (3270 cm^{-1}) is shifted to lower wavenumbers compared to that observed for the monomeric state in chloroform (3451 cm^{-1}), indicating the existence of hydrogen-bonding networks in the assembly (Figure S45). This shifted value is in good agreement with the reported value (3285 cm^{-1}) for H-aggregated porphyrins.^[20a]

Previous studies on stacked Ni^{II} norcorrole dimers elucidated that the effective orbital interactions between face-to-face-stacked norcorroles result in a distinct absorption band in the range of 700–1000 nm.^[18] In contrast, self-assembled **2** exhibited no characteristic absorption band in the NIR region, implying that norcorrole **2** does not form a face-to-face stacking arrangement.

We then estimated the stacking orientation in self-assembled **2** using theoretical calculations. The 3,4,5-trialkoxyphe-nyl moieties were replaced with hydrogen atoms to reduce the computational costs. Two stable conformations, **A** and **B**, with slipped and face-to-face stacking structures, respectively, were obtained from the DFT calculations at the

B97D3/6-31G(d) + SDD level of theory (Figures 5a, 5b). TD-DFT calculations at the CAM-B3LYP/6-31G(d) + SDD level were performed to simulate the absorption spectra of **A** and **B**. In **A**, the slipped π - π stacking should exhibit a weak forbidden transition in the range of 500–900 nm (oscillator strengths $f < 0.0085$) (Figure S37 and Table S6). This absorption feature is in good agreement with the experimental absorption spectrum of assembled **2**. On the other hand, the face-to-face π - π stacking in **B** should exhibit a distinct absorption band around 660 nm, for which the predominant contribution was assigned to the HOMO $\rightarrow$ LUMO + 1 transition ($f = 0.2508$) (Figure S38 and Table S7). However, this situation does not match the experimental spectrum.

To obtain further insights into the self-assembled structure of **2**, variable-temperature ^1H NMR (VT- ^1H NMR) measurements were conducted (Figure S46). Upon cooling of a hot solution of **2** in cyclohexane- d_{12} /benzene- d_6 (13/7) from 343 to 323 K, the pyrrole proton signals shifted from 2.6 ppm to 4.5 ppm. This indicates that the π -systems of **2** are close to each other in the aggregates. The ^1H NMR chemical shifts of the pyrrole protons in **A** and **B** were also simulated using DFT calculations at the B3LYP/6-31G(d) + SDD level of theory (Figure S39). In the face-to-face stacking structure **B**, the pyrrole protons appeared in the aromatic region ($\delta = 6.7\text{--}7.7\text{ ppm}$), while the chemical-shift changes were smaller in the slipped stacking structure **A** ($\delta = 4.5\text{--}5.6\text{ ppm}$). These results also suggest that the Ni^{II} norcorrole unit in assembled **2** is likely to adopt the slipped stacking mode.

Antiaromatic molecules in close proximity should furnish electronically conductive pathways due to their stabilized LUMO and destabilized HOMO levels.^[25] Previously, we have reported that the one-dimensional columnar alignment of Ni^{II} *meso*-dimethylnorcorrole in a slipped parallel manner provides stable electron-conducting pathways.^[17] Thus, the one-dimensional stacking assembly of **2** is expected to exhibit charge-transport properties.

The electronic conduction along an isolated chain configuration of **2** in solution was examined using flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements in cyclohexane/benzene (9/1) with chloranil as a mediator for the photo-induced electron-transfer reactions.^[26] Electrodeless photocarrier injection was performed upon excitation at 355 nm. Upon heating the solution of **2** (70 μM) from 293 to 340 K, the photoconductivity signals gradually decreased and then disappeared abruptly at 340 K (Figure 6a). This result is due to the dissociation of the supramolecular polymer at 340 K, which is consistent with the results observed during the heating process of self-assembled **2** in the UV-Vis-NIR absorption measurements (Figure S47). A maximum $\phi\Sigma\mu_{\text{max}}$ value of $6 \times 10^{-5}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ (ϕ : photo-generation efficiency of the charge carriers; $\Sigma\mu$: sum of the isotropic electron and hole mobility) was recorded for self-assembled **2** in solution. The quantum efficiency of the charge-carrier generation (ϕ) was determined to be 4×10^{-2} for **2** using transient absorption spectroscopy of chloranil radical anions: counter charges as an indicator. At 298 K, the sum of the isotropic electron and hole mobility is $\Sigma\mu = 1 \times 10^{-3}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ for **2**.

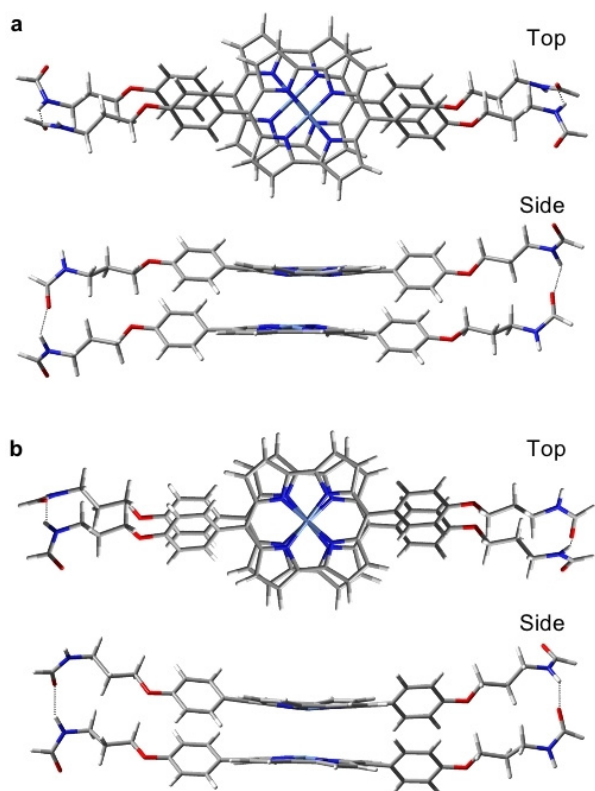


Figure 5. a) Slipped stacking structure **A** and b) Face-to-face stacking structure **B** calculated at the B97D3/6-31G(d) + SDD level of theory; for the calculations, the 3,4,5-trialkoxyphe-nyl moieties were replaced with hydrogen atoms.

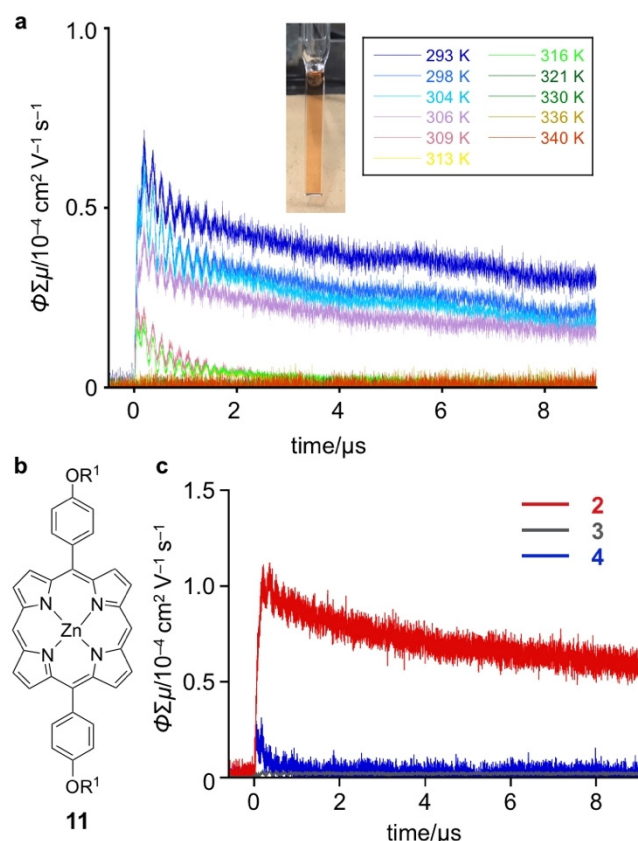


Figure 6. a) Photoconductivity transients of self-assembled **2** in cyclohexane/benzene (9/1) with 10 equiv of chloranil at 293–340 K ($[2] = 70 \mu\text{M}$); inset: Solution sample in a cell with a 3 mm light path. b) Structure of Zn^{II} porphyrin **11**. c) Photoconductivity transients of self-assembled **2** (red), **3** (black), and **4** (blue) in thin films. The solution and solid were excited using Nd:YAG laser pulses (duration: $\approx 5 \text{ ns}$; 355 nm (third harmonics); $1.4 \times 10^{16} \text{ photons cm}^{-2}$).

We also evaluated the charge transport properties of the corresponding aromatic supramolecular polymer consisting of amide-functionalized Zn^{II} porphyrin **11** reported by Takeuchi, Sugiyasu, and co-workers.^[20b] We selected **11** rather than the corresponding Ni^{II} porphyrin as a reference molecule for Ni^{II} norcorrole **2** because the Ni^{II} porphyrin is not suitable for comparison due to its non-planar structure.^[27] To ensure consistency with the measurement conditions used for **2**, the aggregation behavior and structure of **11** in cyclohexane/benzene (9/1) were confirmed using UV-Vis-NIR absorption spectroscopy (Figures S50, S51), TEM (Figure S54), AFM (Figure S55), and FT-IR measurements (Figure S53). Formation of bundled fibers of **11** were observed as is the case of **2**. In addition, the elongation enthalpy (-116 kJ mol^{-1})^[28] and NH stretching band (3267 cm^{-1}) of self-assembled **11** are comparable to those of self-assembled **2**. These results imply that the stacking mode of self-assembled **11** is similar to that of self-assembled **2**. The electronic photoconduction of self-assembled **11** was examined using the FP-TRMC technique (Figure S56). At 297 K, the $\Sigma\mu$ value for self-assembled **11** ($3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was one quarter of that of self-assembled **2**. In addition, the electronic conduction of **11** in solid^[29] was also examined using FP-TRMC measurements revealed that **2**

has a more stable charge carrier transport transportability than **11** (Figure S58).

Finally, photoconductivity measurements were performed for solid samples of **2**, **3**, and **4** (Figure 6c).^[30,31] The TRMC signals were very weak for **3** and **4**. In the crystal of **4**, the distance between the norcorrole π -systems is so long that the effective charge-transport pathway is not formed. In contrast, the maximum $\phi\Sigma\mu_{\text{max}}$ of self-assembled **2** ($1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is comparable to that of *meso*-dimethylnorcorrole Ni^{II} ($7 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^[17] These results demonstrate that the charge transport property is achieved due to close proximity of the norcorrole π -systems. Furthermore, the alignment of the π -stacking assembly via hydrogen bonding is important for the formation of conductive paths along the stacking axis.

Conclusion

We synthesized amide-functionalized norcorrole Ni^{II} complex **2**. Spectroscopic and microscopic measurements revealed that self-assembled **2** forms a one-dimensional array via hydrogen-bonding interactions and π - π stacking. The stacking conformation of the norcorrole π -systems was investigated using VT- ^1H NMR and UV-Vis-NIR analyses, as well as DFT simulations. Importantly, self-assembled **2** exhibits superior charge-transporting ability compared to that of Zn^{II} porphyrin analogue **11**. It should also be noted here that ester- and alkoxy-functionalized Ni^{II} norcorroles **3** and **4** exhibits no charge-transporting abilities. These results demonstrate that the supramolecular polymerization of antiaromatic molecules represents a promising strategy for the development of effective carrier-transport materials.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: antiaromaticity · hydrogen bond · norcorrole · supramolecular polymer · π - π stacking

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- [28] The value was estimated based on the re-heating process. From the cooling process, the enthalpy was calculated to be

–123 kJ mol⁻¹ (Figure S52 and Table S11). The larger elongation enthalpy of **11** than that of **2** could be due to the larger π -surface of **11**.

- [29] The solid sample was prepared by freeze-drying the solution of **11**. The FT-IR peak due to the hydrogen-bonding interactions is similar to that observed in solution (Figure S51).
- [30] The solid sample was prepared by dripping a 70 μ M solution of **3** in cyclohexane/benzene (9/1) onto a thin film and drying slowly at room temperature under reduced pressure.

- [31] The solid sample was prepared by freeze-drying the solution of **2**. The FT-IR peak due to the hydrogen-bonding interactions is similar to that observed in solution (Figure S45).

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