

Realization of Stacked-Ring Aromaticity in a Water-Soluble Micellar Capsule

Si-Yu Liu, Natsuki Kishida, Jinseok Kim, Norihito Fukui, Rie Haruki, Yasuhiro Niwa, Reiji Kumai, Dongho Kim,* Michito Yoshizawa,* and Hiroshi Shinokubo*



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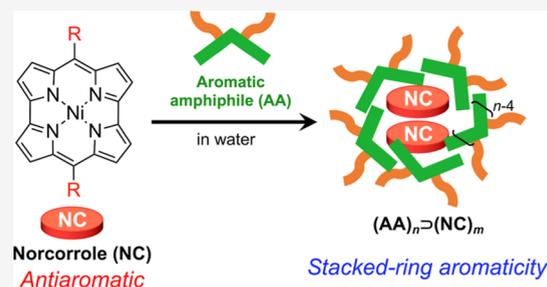
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ABSTRACT: Stacked-ring aromaticity arising from the close stacking of antiaromatic π -systems has recently received considerable attention. Here, we realize stacked-ring aromaticity via a rational supramolecular approach. A nanocapsule composed of bent polyaromatic amphiphiles was employed to encapsulate several antiaromatic norcorrole Ni(II) complexes (NCs) in water. The resulting micellar capsules display high stability toward heating and concentration change. The encapsulation resulted in the appearance of a broad absorption band in the near-infrared region, which is characteristic of norcorroles with close face-to-face stacking. Importantly, a *meso*-isopropyl NC, which does not exhibit π -stacking even in a concentrated solution or the crystalline phase, adopted π -stacking with stacked-ring aromaticity in the supramolecular micellar capsule.



INTRODUCTION

The intermolecular interactions of π -conjugated systems play an important role in the condensed phase.^{1,2} The effective electronic interaction among the constituent molecules realizes unique chemical and physical properties, including high stability, near-infrared (NIR) response, and reversible redox behavior. Consequently, strategies for fine-tuning intermolecular interactions are essential for the rational design of novel bulk materials.

The interaction between stacked antiaromatic π -systems has recently attracted considerable attention. In 2007, Schleyer and co-workers theoretically proposed that stacking of two antiaromatic systems in methano-bridged superphanes eliminates their antiaromaticity, which originates from their effective orbital interactions (Figure 1a).³ This proposal was further supported through a theoretical study by Fowler, which clarified that the three-dimensional π -delocalization switches the ring current from paramagnetic to diamagnetic.⁴ This phenomenon has been known as stacked-ring aromaticity.^{5,6} However, experimental evaluations of stacked-ring aromaticity still remained rare because intrinsically reactive antiaromatic π -systems require kinetic stabilization by bulky peripheral substituents, which inevitably prevent effective orbital interactions.⁷

Norcorrole is a ring-contracted porphyrin that lacks two *meso*-carbons relative to a regular porphyrin.⁸ According to the Hückel rule, norcorrole exhibits antiaromaticity due to its 16 π -electronic circuit and planar structure (Figure 1b). Our group has reported the synthesis of a stable norcorrole Ni(II) complex (NC).⁹ Subsequently, we attempted the synthesis of

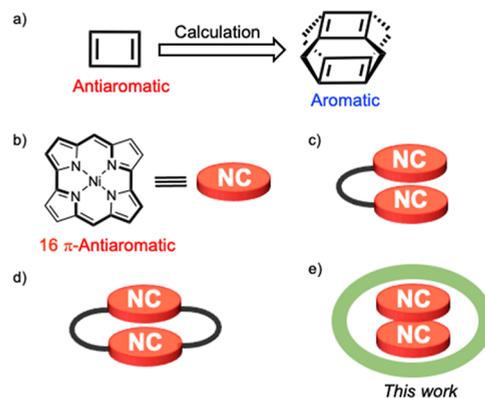


Figure 1. Strategies for the generation of stacked-ring aromaticity. (a) Cyclobutadiene dimer. (b) 16 π -antiaromatic norcorrole NC. (c,d) Previously reported covalently linked stacked norcorrole dimers. (e) Generation of stacked-ring aromaticity through a supramolecular approach within a molecular capsule (this work).

NCs with less bulky peripheral substituents in order to facilitate π - π stacking in the solid state.¹⁰ Recently, we have achieved stacked-ring aromaticity by tethering two norcorrole

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units using covalent linkers (Figure 1c,d).¹¹ These norcorrole dimers exhibit characteristic absorption bands in the NIR region, which originate from the mutual orbital interactions between the two closely stacked subunits. However, the current strategy to achieve stacked-ring aromaticity consists only of this tethering approach, which requires the elaborate synthesis of norcorrole dimers.

Here, we report the encapsulation of antiaromatic norcorroles via a supramolecular approach to accomplish stacked-ring aromaticity (Figure 1e).¹² Amphiphile **1**, which consists of a bent bisanthracene framework with two trimethylammonium groups, forms capsular assemblies ($(1)_n$) in water to provide a polyaromatic shell (diameter: ~ 1 nm) through aromatic–aromatic interactions (Figure 2a).¹³ The

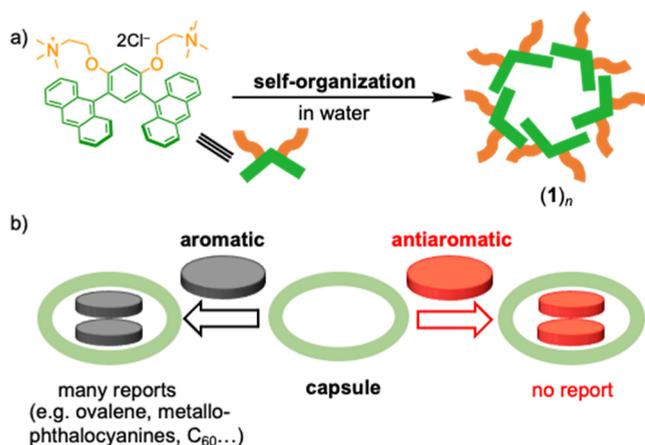


Figure 2. (a) Formation of a micellar capsule $(1)_n$ from polyaromatic amphiphile **1**. (b) Encapsulation of aromatic and antiaromatic π -systems in $(1)_n$.

aqueous host is capable of encapsulating a wide range of hydrophobic π -systems, such as polycyclic aromatic hydrocarbons (e.g., ovalene and dicoronylene), metallophthalocyanines, and fullerene (Figure 2b).¹⁴ The resulting host–guest complexes are highly soluble in water and stable under ambient conditions. However, the encapsulation of antiaromatic π -systems as well as their water solubilization has not been achieved to date owing to their relatively large frameworks (>1 nm) and difficulty in attaching several hydrophilic groups, respectively.

RESULTS AND DISCUSSION

Facile Preparation of Host–Guest Complexes with Norcorroles. Manual grinding of polyaromatic amphiphile **1** with *meso*-mesityl NC **2a**,⁹ *meso*-phenyl NC **2b**,^{11a} and *meso*-isopropyl NC **2c**^{10b} readily furnished water-soluble host–guest complexes (Figure 3). A typical procedure is briefly described here. A mixture of norcorrole **2a** (1.0 μ mol) and **1** (1.0 μ mol) was ground for 5 min using a mortar and pestle. The resulting solid was dissolved in H₂O (1.0 mL) at room temperature, and the suspension thus obtained was centrifuged (gravitational force: 16,000g) for 30 min. After the removal of excess **2a** using a membrane filter (pore size: 200 nm), a clear brown solution of $(1)_n \supset (2a)_m$ was obtained.¹⁵ It is worth noting that the use of the conventional surfactant sodium dodecyl sulfate instead of **1** resulted in insufficient encapsulation of *meso*-phenyl NC **2b**, with ca. 21 times lower efficiency (Figure S11). This result indicates that the presence of amphiphile **1** bearing

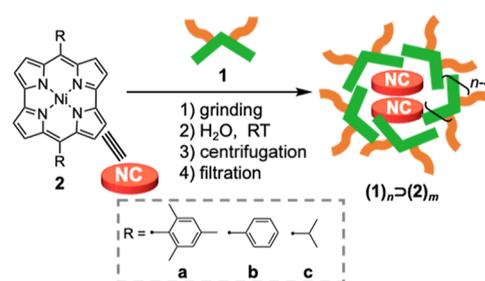


Figure 3. Preparation of host–guest complexes $(1)_n \supset (2)_m$ in water.

polyaromatic panels is necessary for the effective encapsulation of NCs.

The size and compositions of host–guest complexes $(1)_n \supset (2a)_m$, $(1)_n \supset (2b)_m$, and $(1)_n \supset (2c)_m$ were analyzed using dynamic light scattering (DLS) and ¹H NMR spectroscopy. The former revealed the selective formation of small particles with narrow size distributions and the core diameters of $(1)_n \supset (2a)_m$ (2.2 nm), $(1)_n \supset (2b)_m$ (2.6 nm), and $(1)_n \supset (2c)_m$ (3.4 nm) (Figure 4). These diameters are comparable to or slightly larger than that of a previously reported capsule with encapsulated phthalocyanine (1.9 nm),¹⁶ in which two phthalocyanine molecules are encapsulated by six molecules of **1**. The guest ¹H NMR signals disappeared due to the restricted dynamic motion of the encapsulated guests in the confined space of the capsule. This phenomenon is typical for the anthracene-based micellar host $(1)_n$.^{13a} To determine the host–guest ratio (n/m) of host–guest complexes, water in each solution was removed via freeze-drying. The resulting solids were dissolved in DMF-*d*₇ containing 1% trifluoroacetic acid (TFA). Under these conditions, guest molecules **2a**, **2b**, and **2c** dissociate from capsule $(1)_n$. The host–guest ratio (n/m) was determined based on the integral ratio of the sharp ¹H NMR signals for $(1)_n \supset (2a)_m$ (5:1), $(1)_n \supset (2b)_m$ (2.5:1), and $(1)_n \supset (2c)_m$ (1.6:1) (Figures S4–S6).

Spectral Analysis of Host–Guest Complexes. The UV–vis–NIR absorption spectra of $(1)_n \supset (2a)_m$, $(1)_n \supset (2b)_m$, and $(1)_n \supset (2c)_m$ in water are shown in Figure 5. The absorption spectrum of $(1)_n \supset (2a)_m$ is almost identical to the simple sum of the absorption spectra of **1** in water and **2a** in CH₂Cl₂, indicating that there are no intermolecular interactions between encapsulated molecules of NC **2a**. The forbidden absorption tailing to about 1500 nm is characteristic of the NC monomer.⁹ In sharp contrast, $(1)_n \supset (2b)_m$ and $(1)_n \supset (2c)_m$ exhibit new broad absorption bands in the NIR region [$(1)_n \supset (2b)_m$: $\lambda_{\max} = 870$ nm; $(1)_n \supset (2c)_m$: $\lambda_{\max} = 824$ nm], which are a diagnostic feature of face-to-face stacked norcorroles.¹¹ These results suggest that *meso*-phenyl NC **2b** and *meso*-isopropyl NC **2c** form π -stacking assemblies with intermolecular orbital interactions in the supramolecular micellar capsules. The absence of the NIR absorption band in the case of $(1)_n \supset (2a)_m$ is attributed to interruption of the π -stacking by the bulky mesityl substituents. The absorption spectra of $(1)_n \supset (2a)_m$, $(1)_n \supset (2b)_m$, and $(1)_n \supset (2c)_m$ in water were also compared with those of **2a**, **2b**, and **2c** in the solid state (Figure S15). For NCs **2a** and **2b**, their absorption spectra in the solid state were similar to those of encapsulated molecules in water, indicating the formation of π -stacked aggregates of **2b** in capsule, which is observed in the solid state. The broad absorption band at 824 nm in the absorption spectra of $(1)_n \supset (2c)_m$ in water was not evident in the solid-state absorption spectrum, which would suggest that the

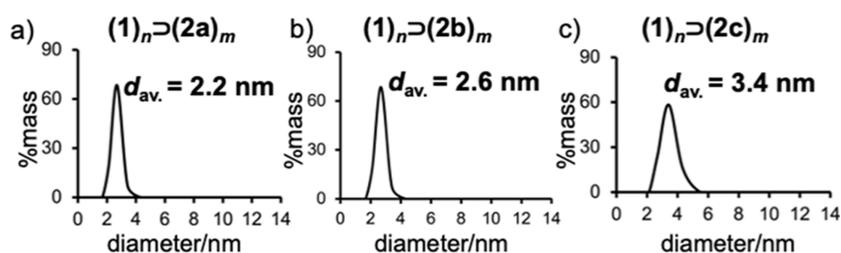


Figure 4. DLS-derived size distributions of the host-guest complexes (a) $(1)_n \supset (2a)_m$, (b) $(1)_n \supset (2b)_m$, and (c) $(1)_n \supset (2c)_m$.

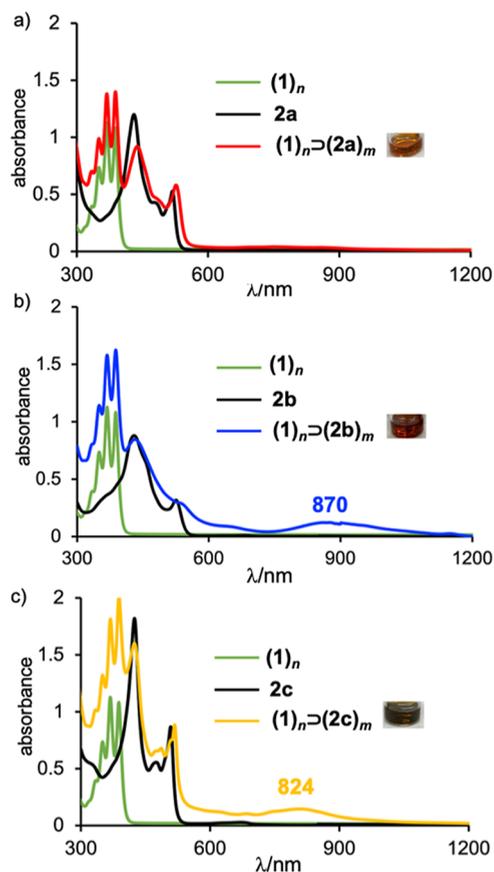


Figure 5. UV-vis-NIR absorption spectra of host capsule $(1)_n$ in water (concentration: 1.0 mM based on **1**), NCs **2a–2c** in CH_2Cl_2 (concentration: 0.1 mM), and host-guest complexes $(1)_n \supset (2a–2c)_m$ in water (concentration: 1.0 mM based on **1**) at room temperature. (a) Spectra of $(1)_n$, **2a**, and $(1)_n \supset (2a)_m$. (b) Spectra of $(1)_n$, **2b**, and $(1)_n \supset (2b)_m$. (c) Spectra of $(1)_n$, **2c**, and $(1)_n \supset (2c)_m$.

assembly of **2c** in a micellar capsule is different from that in solids.

We also measured the femtosecond transient absorption (fs-TA) spectra of $(1)_n \supset (2a)_m$ and $(1)_n \supset (2b)_m$ in water to compare the results with structurally well-defined norcorroles (Figure 6). The TA spectrum of $(1)_n \supset (2a)_m$ exhibited a sharp and derivative-like TA band around 550 nm. This spectral feature is well matched with the TA spectra of a monomeric Ni(II) norcorrole in solution.^{11b} It is well known that the derivative-like spectral feature represents the (d,d) state contribution in the excited-state dynamics of Ni(II) porphyrinoids.¹⁷ On the other hand, broad and dominant excited-state absorption (ESA) bands were observed from 500 to 770 nm in the TA spectrum of $(1)_n \supset (2b)_m$. This spectral

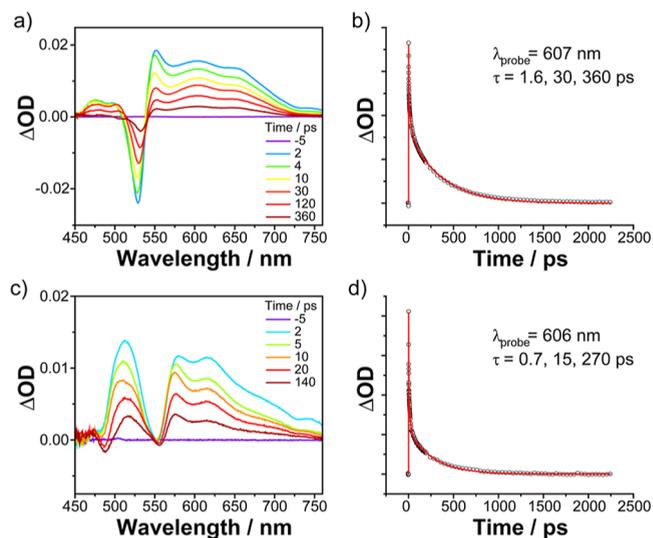


Figure 6. (a) TA spectra and (b) decay profile of $(1)_n \supset (2a)_m$. (c) TA spectra and (d) decay profile of $(1)_n \supset (2b)_m$.

feature is in line with that of the face-to-face stacked norcorrole cyclophane in solution.^{11b} The broad ESA bands could indicate an increased density of electronic states arising from the electronic interactions between the adjacent NCs in the capsule.

Structural Analysis of Host-Guest Complexes. The structure of $(1)_n \supset (2b)_m$ was simulated using molecular mechanics (MM) calculations.¹⁸ Initially, double- and triple-decker stacked norcorroles were optimized via density functional theory (DFT) calculations at the $\omega\text{B97XD}/6\text{-31G(d)}+\text{SDD}$ level of theory. These stacked oligomers wrapped with amphiphile **1** were subjected to MM calculations. Diameters were simulated for host-guest complexes $(1)_5 \supset (2b)_2$ (2.4 nm) and $(1)_8 \supset (2b)_3$ (2.7 nm) (Figure 7). The hydrophobic dimer $(2b)_2$ and trimer $(2b)_3$ are both completely encircled by the polyaromatic shell

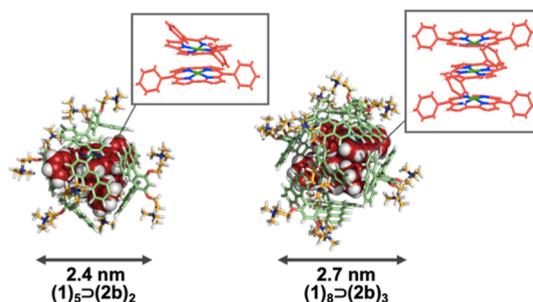


Figure 7. Optimized structures for $(1)_5 \supset (2b)_2$ and $(1)_8 \supset (2b)_3$ and their highlighted guest stacking.

decorated with multiple hydrophilic side chains. The particle size analysis via DLS and ^1H NMR spectroscopy suggests that these two complexes are dominant in aqueous solution.

To obtain information on the local structure around the Ni(II) center of the host–guest complexes, we conducted X-ray absorption fine structure (XAFS) analysis of $(1)_n \supset (2a)_m$ and $(1)_n \supset (2b)_m$ using synchrotron radiation (Figure S10). The observed peaks were weak except the peak due to the nearest coordinating nitrogen atoms. Consequently, it is difficult to determine the detailed π -stacking orientation of $(2b)_m$ in the micellar capsule on the basis of the XAFS experiments. Considering the aforementioned results of steady-state absorption and TA analyses, the weak absorption peaks in XAFS spectra could be due to the dispersity in the distance between Ni(II) centers in π -stacking aggregates of NCs.

Comparison with Encapsulation of a Porphyrin Analogue. To further confirm the stacked conformation of antiaromatic π -systems in capsule $(1)_n$, the encapsulation of Ni(II) 5,15-diphenylporphyrin **3** in a manner similar to that of **2** was also examined for comparison. The core diameter of the obtained host–guest complex $(1)_n \supset (3)_m$ was estimated to be 2.5 nm based on a DLS analysis (Figure 8a). Its host–guest

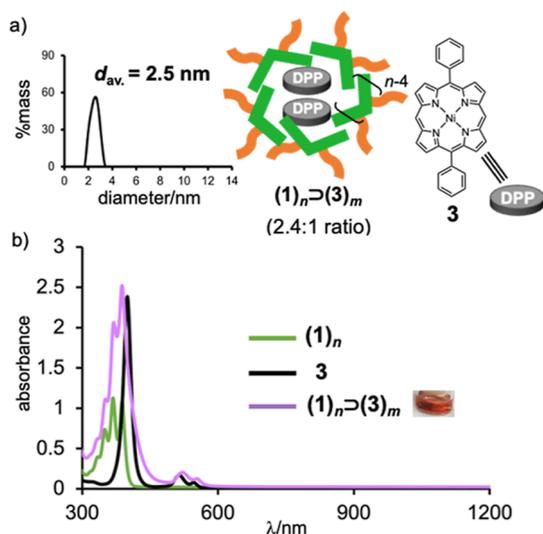


Figure 8. (a) DLS-derived size distribution of $(1)_n \supset (3)_m$. (b) UV-vis-NIR absorption spectra of host capsule $(1)_n$ (solvent: H_2O ; concentration: 1.0 mM based on **1**), **3** (solvent: CH_2Cl_2 ; concentration: 0.1 mM), and host–guest complexes $(1)_n \supset (3)_m$ (solvent: H_2O ; concentration: 1.0 mM based on **1**) at room temperature.

ratio was confirmed to be 2.4:1 by ^1H NMR analysis (Figure S7). These values are almost the same as those for $(1)_n \supset (2b)_m$. The Soret band of **3** was blue-shifted ($\Delta\lambda_{\text{max}} = -12$ nm) upon encapsulation by the present micellar capsule compared to that of monomeric **3** in CH_2Cl_2 , suggesting that the encapsulated porphyrins form an H-type aggregate with face-to-face stacking (Figures 8b and S9).¹⁹ Considering the structural similarity between **2b** and **3**, the corresponding host–guest complexes $(1)_n \supset (2b)_m$ and $(1)_n \supset (3)_m$ should exhibit similar assemblies. Consequently, the spectroscopic features of $(1)_n \supset (3)_m$ suggest that norcorrole **2b** also adopts face-to-face stacking in the inner cavity of the capsules, thus supporting the results of the MM simulations. It is worth noting that $(1)_n \supset (3)_m$ exhibits no new absorption band in the

NIR region, which indicates a lack of intermolecular orbital interactions in the capsule. This is in sharp contrast to $(1)_n \supset (2b)_m$, which exhibited specific absorption bands owing to the effective intermolecular orbital interactions.

High Stability of Host–Guest Complexes in Water. The stability of host–guest complexes $(1)_n \supset (2b)_m$ and $(1)_n \supset (2c)_m$ was examined by monitoring their UV-vis-NIR absorption spectra. $(1)_n \supset (2b)_m$ and $(1)_n \supset (2c)_m$ both exhibit high stability toward concentration change (Figure 9).

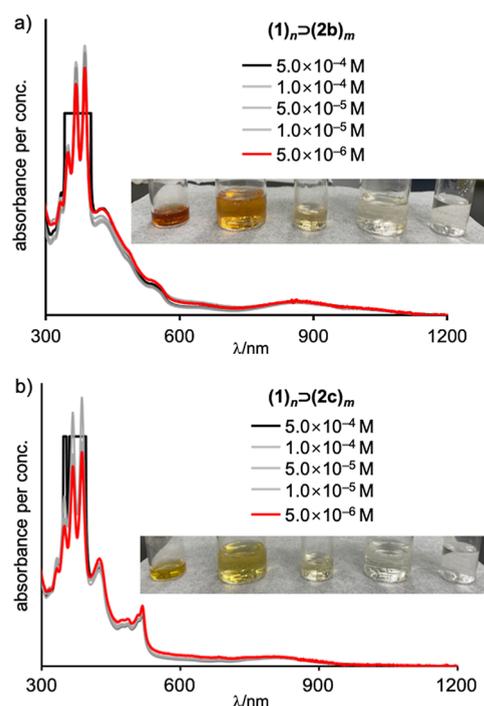


Figure 9. Concentration-dependent UV-vis-NIR absorption spectra of (a) $(1)_n \supset (2b)_m$ and (b) $(1)_n \supset (2c)_m$ (solvent: H_2O ; concentration: based on **1**) at room temperature.

The π -stacked conformers are persistent even at quite low concentrations ($<5.0 \times 10^{-6}$ M), indicating efficient guest–guest and host–guest interactions. Furthermore, complex $(1)_n \supset (2c)_m$ remained unchanged after heating at 80°C for more than 1 week (Figure S13). The UV-vis absorption spectrum of $(1)_n \supset (2b)_m$ changed slightly at ~ 450 nm after heating to 80°C , but the change in the long-wavelength absorption was negligible (Figure S12a). Furthermore, the DLS results suggested that the average diameter of $(1)_n \supset (2b)_m$ changed from 2.6 to 5.1 nm (Figure S12b,c). These results indicate that fusion of the micellar capsule aggregates occurs to form larger capsules and that the face-to-face stacked assemblies of *meso*-phenyl NC **2b** still exist in the merged capsules. Unlike the NC micellar capsules, $(1)_n \supset (3)_m$ exhibits low stability toward heating. Guest molecules of **3** were gradually released from the capsules after heating (Figure S14).

Instability of Stacked Norcorroles in Organic Solvents without Encapsulation. We evaluated the advantages of the current supramolecular approach in achieving stacked-ring aromaticity. *meso*-Phenyl NC **2b** adopts a triple-decker stacking structure in the solid state.^{11a} In solution, however, the characteristic absorption band around 850 nm only appeared at higher concentrations than 1.0×10^{-3} M in CH_2Cl_2 (Figure 10a). This result suggests that very high

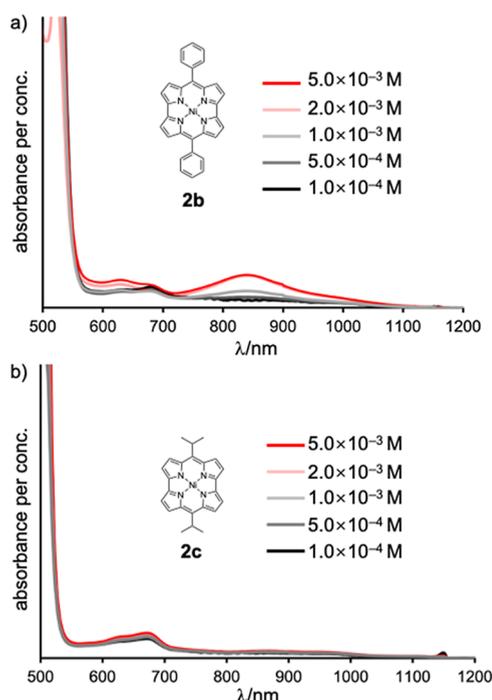


Figure 10. Concentration-dependent UV-vis-NIR absorption spectra of (a) **2b** and (b) **2c** (solvent: CH_2Cl_2) at room temperature.

concentrations are required to induce π - π stacking of **2b** in organic solvents. The situation is more clear-cut for *meso*-isopropyl NC **2c**, which does not form π -stacking structures even in saturated solutions (Figure 10b). In sharp contrast, **2c** exhibited stacked-ring aromaticity in the micellar capsule. These results demonstrate that the supramolecular approach is advantageous (1) to realize stacked-ring aromaticity in even dilute solutions and (2) to force intrinsically nonstacking antiaromatic molecules to exhibit stacked-ring aromaticity.

CONCLUSIONS

We have synthesized micellar capsules that contain several antiaromatic norcorrole NC in water. The resulting micellar capsules display high stability toward concentration change and heating. Unique spectroscopic changes were observed for *meso*-phenyl NC **2b** and *meso*-isopropyl NC **2c** in the capsules due to the encapsulation-induced face-to-face π -stacking orientation of the norcorrole units, which was supported by experiments and theoretical calculations. The present study thus provides a facile strategy to realize π - π stacking of antiaromatic compounds in solution without laborious synthesis as well as a novel way to open up antiaromatic chemistry in water. The development of nanocapsules that consist of discrete π -stacking assemblies of norcorroles is our next target for the systematic understanding of the intermolecular interactions among antiaromatic norcorroles.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c08795>.

Instrumentation, materials, additional experimental details, methods, and calculation details (PDF)

AUTHOR INFORMATION

Corresponding Authors

Dongho Kim – Spectroscopy Laboratory for Functional π -Electronic Systems and Department of Chemistry, Yonsei University, Seoul 03722, Korea; orcid.org/0000-0001-8668-2644; Email: dongho@yonsei.ac.kr

Michito Yoshizawa – Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama 226-8503, Japan; orcid.org/0000-0002-0543-3943; Email: yoshizawa.m.ac@m.titech.ac.jp

Hiroshi Shinokubo – Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, and Integrated Research Consortium on Chemical Sciences (IRCCS), Nagoya University, Nagoya, Aichi 464-8603, Japan; orcid.org/0000-0002-5321-2205; Email: hshino@chembio.nagoya-u.ac.jp

Authors

Si-Yu Liu – Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, and Integrated Research Consortium on Chemical Sciences (IRCCS), Nagoya University, Nagoya, Aichi 464-8603, Japan

Natsuki Kishida – Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama 226-8503, Japan

Junseok Kim – Spectroscopy Laboratory for Functional π -Electronic Systems and Department of Chemistry, Yonsei University, Seoul 03722, Korea

Norihito Fukui – Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, and Integrated Research Consortium on Chemical Sciences (IRCCS), Nagoya University, Nagoya, Aichi 464-8603, Japan; PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan; orcid.org/0000-0002-0466-0116

Rie Haruki – Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba 305-0801, Japan

Yasuhiro Niwa – Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba 305-0801, Japan; orcid.org/0000-0001-5808-5594

Reiji Kumai – Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba 305-0801, Japan

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/jacs.2c08795>

Notes

The authors declare no competing financial interest.

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