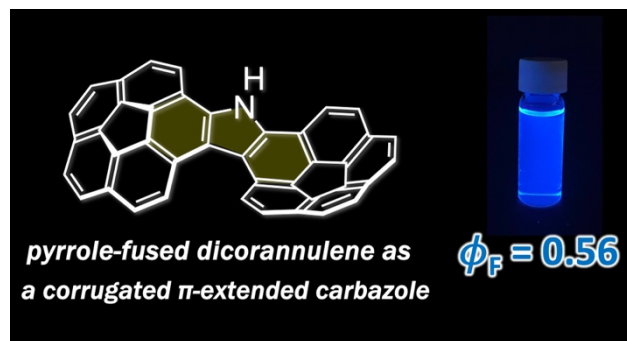


Synthesis of a Highly Luminescent Pyrrole-fused Dicorannulene as a Corrugated π -Extended Carbazole.

Koki Kise, Aoi Nakagawa, Shu Seki, and Takayuki Tanaka*



ABSTRACT: A pyrrole-fused dicorannulene was designed and synthesized via Pd-catalyzed reactions. This molecule can be regarded as a corrugated π -extended carbazole, which exhibited efficient blue fluorescence ($\Phi_F = 0.56$) in contrast to fairly non-emissive pristine corannulene. In addition, deprotonation of the pyrrolic NH by tetrabutylammonium hydroxide gave stable anionic species with a perturbed optical response. Its tetrabutylammonium salt was isolable under ambient conditions owing to the extensive charge delocalization onto the π -extended chromophore.

Superbenzene (SB) is one of π -extended benzenes that retains the same D_{6h} symmetry, such as coronene and hexa-*peri*-hexabenzocoronene (HBC).¹ Although the optical properties of SBs themselves have not been considered suitable for efficient emitters due to the symmetrically-forbidden nature of their low-energy electronic transitions, a considerable number of such supersized chromophores have recently been developed to harvest their potentials for optical applications. These can be classified into i) peripherally substituted HBC derivatives² and ii) HBC-embedded polycyclic chromophores.³ The former includes peripherally aminated HBC derivatives in which symmetry-allowed π - π^* transition as well as intramolecular charge transfer effect impart enhanced optical response. As the latter examples, superhelicenes (SHs) have recently attracted attention in view of their significant twisting and perturbed electronic properties. Jux et al. reported a series of superhetera[7]helicenes **1a–e** which indeed exhibited high fluorescence quantum yields up to $\Phi_F = 0.86$ for **1c** (Figure 1).³ The hetera[7]helicene scaffold exhibits optical stability regardless of the embedded heteroatoms, allowing enantiomeric separation for **1a–d**.

A similar molecular design concept can be applied to incorporate corannulene segments as an electron-deficient bowl-shaped π -scaffold. Pristine corannulene is only weakly emissive ($\Phi_F = 0.013$ in CH_2Cl_2),⁴ while peripherally aminated corannulenes have recently been reported to exhibit significantly perturbed optical properties.^{5–7} Among them, N,N-diphenylaminocorannulene⁵ and indole-fused

corannulene^{7a} have been reported to be efficient blue emitters. We envisioned that pyrrole-fused dicorannulene could be regarded as a π -extended carbazole with bowl-shaped structures. This molecular framework formally includes an aza[5]helicene segment, although it does not exhibit substantial helicene-like behavior. When HBC units are used as wings, the resulting structure inevitably adopts a helical conformation, thereby making it indistinguishable from SHs.^{3,8} The quantum calculation predicted that the helical inversion needs only 3.4 kcal/mol, that is lower than the bowl-to-bowl inversion barrier of pristine corannulene (ca. 12.5 kcal/mol).⁹ The energy-minimized structure of this molecule shows two bowl-fragments pointing in an opposite direction (*i.e.* anti-type). Inspired by our recent successful synthesis of indole-fused corannulenes via palladium-catalyzed intramolecular direct arylation,^{7a} the synthesis could be achieved from nitrogen-linked corannulene dimer (Scheme 1). Only a handful of fused corannulene oligomers have been reported,^{10,11} however, their optical properties have remained largely unexplored. In this paper, we report the synthesis, structure and luminescent properties of pyrrole-fused dicorannulene. Interestingly, it exhibits the highest fluorescence quantum yield ($\Phi_F = 0.56$) among the series of peripherally fused corannulenes.¹² In addition, optical tuning was achieved via deprotonation of the pyrrolic NH group. The resulting salt was sufficiently stable to be isolated under ambient conditions owing to extensive charge delocalization onto the π -extended chromophore.

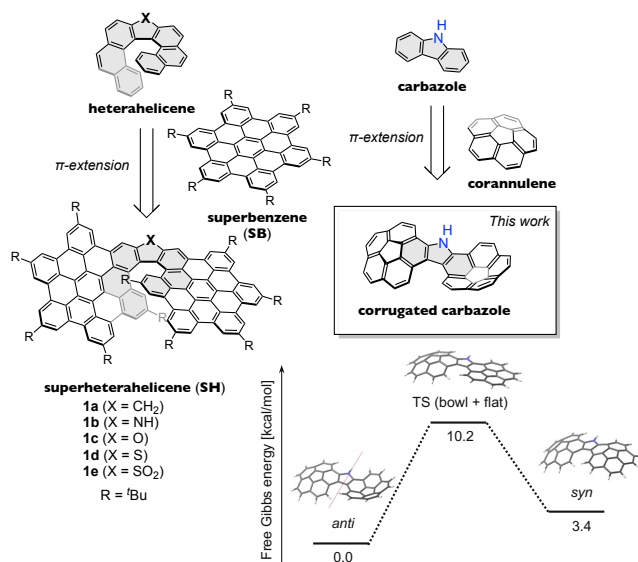
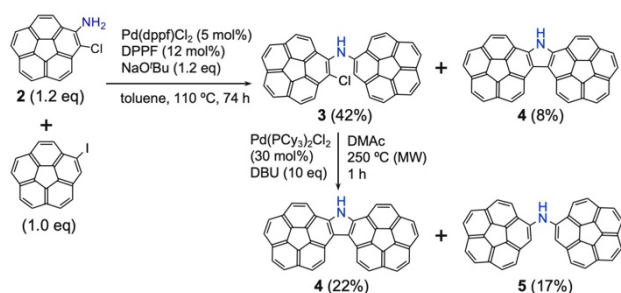


Figure 1. Superheterahelicenes and corrugated carbazole. The bowl-inversion energy diagram is shown below. Calculation level; B3LYP-D3(BJ)/def2-SVP.

Scheme 1. Synthesis of **4** and **5**.



1-Amino-2-chlorocorannulene (**2**) was coupled with iodo-corannulene¹³ by utilizing Pd-catalyzed Buchwald-Hartwig amination to afford dimer **3** in 42% yield. In this reaction, surprisingly, the target compound **4** was also obtained (8%). The isolated product **3** was subjected to the reaction conditions for intramolecular C-H arylation under microwave irradiation,¹⁴ which gave **4** in 22% yield along with the protodechlorinated product **5** (17% yield). The high-resolution mass spectrometry of **4** and **5** revealed their molecular ion peaks at $m/z = 511.1350$ (calcd. for $C_{40}H_{17}N = 511.1356$ [M]⁺) and $m/z = 513.1516$ (calcd. for $C_{40}H_{19}N = 513.1512$ [M]⁺), respectively. Unfused dimer **5** was well soluble in $CDCl_3$ and each proton on both corannulene units was observed as an equivalent signal at room temperature, indicating that C-N bonds rotate faster than the NMR time scale (Figure S4-5). In contrast, **4** was hardly soluble in halogenated solvents, but was soluble in THF and DMSO. This solubility profile resembles that of tetraaza[8]circulenes, in which the outer-pointing NH sites form hydrogen-bonds with THF or DMSO, to allow the molecule sufficiently soluble in these solvents in spite of the absence of bulky solubilizing substituents.¹⁵ Thus, the 1H NMR spectrum of **4** was measured in THF- d_8 (Figure S4-7). A broad singlet was observed at 12.85 ppm due to the NH proton and four pairs of doublets were observed in the range of 9.16–7.86 ppm due to the protons on the corannulene scaffolds. Single crystals of **4** suitable for the X-ray diffraction (XRD) analysis were obtained by vapor diffusion of n -hexane into its THF solution, and its structure was

unambiguously determined (Figure 2a). Dimer **4** adopts an *anti*-form, where the convex face of one corannulene unit opposes that of the other (Figure 2b). Specifically, the rim bonds at pyrrole-fused sides are slightly longer (1.428(2) and 1.425(2) Å) than that of the pristine corannulene (1.39 Å). The bowl-depths of the two corannulene units (0.862 and 0.858 Å) are similar to that of the pristine corannulene (0.87 Å). According to the definition of bowl chirality,¹⁶ both enantiomers possessing *PP* and *MM* bowl chiralities were observed in the unit cell (Figure 2c). **4** stacked in a concave-to-convex columnar fashion along the b -axis without solvent molecules (Figure S7-1). This densely packed structure and the absence of solvent molecules would suggest a potential application for efficient carrier transporting in the solid-state.¹⁷

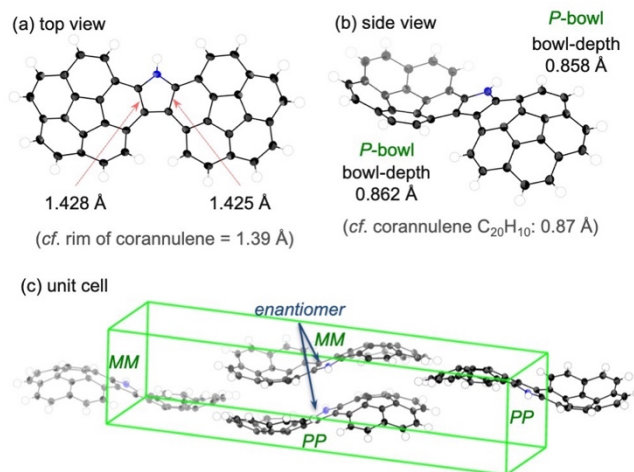


Figure 2. X-Ray crystal structure of **4**. (a) Top view, (b) side view, and (c) unit cell. The thermal ellipsoids: 50% probability level.

The UV/vis absorption and emission spectra of **4** and **5**, as well as that of the pristine corannulene in THF are shown in Figure 3 and the data summarized in Table 1. Unfused dimer **5** exhibits broad structureless absorption and fluorescence spectra with a large Stokes shift of 4000 cm^{-1} . This pronounced shift is attributed to structural relaxation toward a twisted polarized S_1 state.¹⁸ It was supported by the DFT-optimized structure in the S_1 state where the torsion angles around the C-N bonds are 5.98° and 93.46°, associated with the C-N bond lengths of 1.326 and 1.448 Å (Figure S9-4). In that structure, the corannulene unit co-planarized with NH moiety is negatively polarized and the other is positively polarized as seen in its electrostatic potential (ESP) map. On the other hand, fused dimer **4** shows mirror-imaged absorption and fluorescence spectra with small Stokes shift (880 cm^{-1}), reflecting its rigidified structure. Fused dimer **4** and nitrogen-linked dimer **5** show significantly larger fluorescence quantum yields compared with the pristine corannulene. Notably, **4** shows the highest quantum yield ($\Phi_F = 0.56$ in THF) among nitrogen-doped corannulenes. The fluorescence lifetime was measured by the time-correlated single-photon counting (TCSPC) technique to be 5.5 and 5.8 ns for **4** and **5**, respectively. The calculated radiative decay rate constant of **4** ($k_r = 1.0 \times 10^8 s^{-1}$) is ~50 times larger than that of the pristine corannulene ($k_r = 0.022 \times 10^8 s^{-1}$), which mainly contributes to the much higher quantum yield of **4**. Notably, the fluorescence quantum yield and lifetime remained essentially unchanged when dispersed in the PMMA

matrix ($\Phi_F = 0.51$, $\tau = 4.9$ ns). In contrast, the solid-state emission was mostly quenched ($\Phi_F = 0.028$) due to the aggregation-caused quenching (Figure S5-5). The large fluorescence quantum yield of **4** is also consistent with a larger oscillator strength of S_1 - S_0 transition at its S_1 -equilibrium structure ($f = 0.290$), compared with the pristine corannulene ($f = 0.0012$), as reflected by their molar extinction coefficients (Figure S9-3).

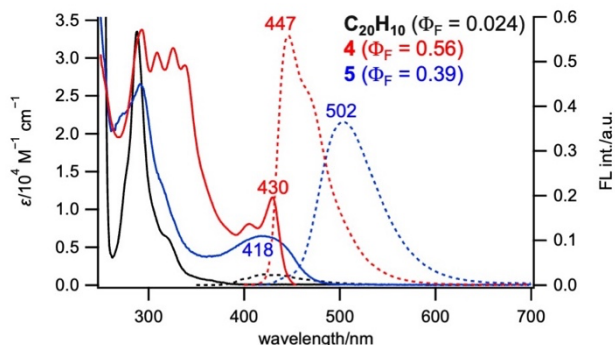


Figure 3. Electronic absorption (solid lines) and fluorescence (dashed lines) spectra of **4** (red), **5** (blue), and pristine corannulene ($C_{20}H_{10}$; black) in THF at room temperature.

Table 1. Summary of the optical parameters of the pristine corannulene ($C_{20}H_{10}$), **4**, and **5** in THF at room temperature.

compd	Φ_F	τ_F [ns]	k_r [10^8 s $^{-1}$]	k_{nr} [10^8 s $^{-1}$]	Stokes shift [cm $^{-1}$]
$C_{20}H_{10}$	0.024	11.0	0.022	0.89	-[a]
4	0.56	5.5	1.0	0.80	880
5	0.39	5.8	0.66	1.1	4000

[a] not calculated due to forbidden HOMO-LUMO transition.

The redox potentials were determined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) (Figure S6-1). Unfused dimer **5** displayed two irreversible oxidation waves at 0.41 and 0.76 V, and two irreversible reduction waves at -2.42 and -2.66 V. Fused dimer **4** showed two quasi-reversible first and second reduction waves at -2.35 and -2.60 V, respectively, and an irreversible oxidation wave observed around 0.4 V. In both cases, the irreversibility in the oxidation event may be attributed to the facile deprotonation of the NH sites, since the acidity of the NH site may be enhanced upon oxidation. After extensive investigation into the functionalization of the NH site of **4**, we found that the anionic state of **4** was highly stable. Indeed, titration with tetrabutylammonium fluoride (TBAF) in THF displayed distinct spectral changes associated with isosbestic points at around 350 and 430 nm (Figure S8-1). The spectral change saturated upon addition of 5.0 equivalents of TBAF to a solution of **4** in THF (ca. 2.7×10^{-5} M $^{-1}$). Essentially the same change was observed upon addition of tetrabutylammonium hydroxide (TBAOH). The spectral change was more straightforward as the change saturated upon addition of ca. 1.4 eq. of TBAOH (Figure 4). In the anionic state, the absorption and emission peaks were substantially red-shifted to 510 and 550 nm, respectively. The

deprotonation behavior was also monitored in the 1H NMR spectrum. Upon the addition of 1.0 eq. of TBAOH to a solution of **4** in THF- d_8 (ca. 14 mM), a peak due to the NH disappeared and other peaks were shifted (Figure S8-3). Finally, single crystals suitable for the XRD analysis were obtained and the structure of the anion (namely, **4** $\cdot$ TBA $^+$) was unambiguously revealed (Figure 5). The *anti*-type arrangement was kept with slightly deeper bowl depth values (0.880 and 0.877 Å) compared with those of neutral **4**. The C—C bond between two corannulene units is slightly shorter (1.424 Å) and the CNC angle becomes smaller upon deprotonation from 110.5° to 106.6°. These changes are also seen in the DFT optimized structures (Figure S7-3). The electronic state of the anion was further investigated computationally. The electrostatic potential map displayed an effectively delocalized electron density. NICS(0)¹⁹ and ACID²⁰ calculations showed essentially the same aromaticity indices upon deprotonation (Figure S9-8 and S9-9). Thus, the remarkable stability of **4** $\cdot$ TBA $^+$ might be attributable to the well-delocalized charge onto the π -extended chromophore as well as steric circumstance around the N site.

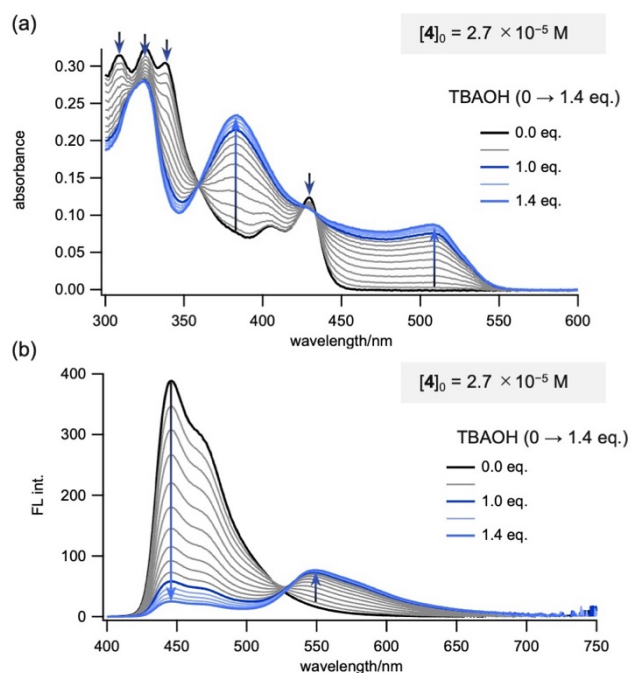


Figure 4. Titration of **4** with TBAOH in THF monitored by (a) UV-vis absorption and (b) fluorescence spectra.

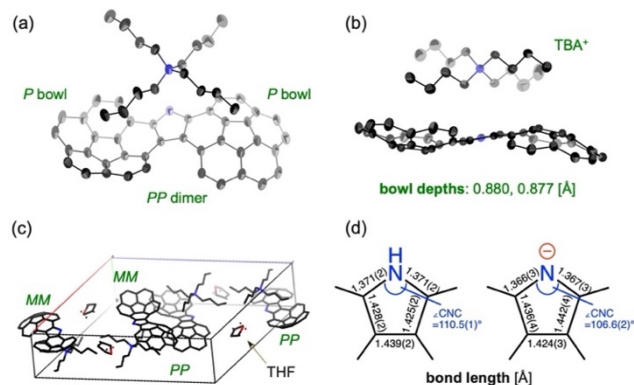


Figure 5. X-Ray crystal structure of **4**·TBA⁺. (a) Top view, (b) side view, (c) unit cell, and (d) selected bond lengths and angles in comparison with those of **4**. The thermal ellipsoids: 50% probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

In conclusion, the pyrrole-fused dicorannulene **4** was synthesized and its characteristic properties were elucidated through various techniques. Notably, **4** exhibits enhanced photoluminescence properties, demonstrating effectiveness of π -extended chromophore design. Furthermore, a stable anionic species of **4** was isolated, attributed to the well-delocalized charge distribution across the extended π -system. The optical properties of **4** can be modulated substantially upon the addition of bases. Further efforts to explore corannulene-embraced π -systems are actively in progress in our laboratory.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedure and characterization data (including HRMS, ¹H and ¹³C NMR spectra, absorption and emission spectra and computational results of **4** and **5**) and single-crystal X-ray analysis of **4** and **4**·TBA⁺.

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Notes

The authors declare no competing financial interest.

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