TITLE:
Dibenzodiazapyracylenes: Doubly N-Doped Cyclopenta-Fused Polycyclic Molecules That Exhibit High Carrier Mobility

AUTHOR(S):
Morimoto, Yuki; Koo, Yun Hee; Otsubo, Kazuya; Kitakado, Hidetsugu; Seki, Shu; Osuka, Atsuhiro; Tanaka, Takayuki

CITATION:

ISSUE DATE:
2022-03

URL:
http://hdl.handle.net/2433/269420

RIGHT:
This is the peer reviewed version of the following article: [Y. Morimoto, Y. H. Koo, K. Otsubo, H. Kitakado, S. Seki, A. Osuka, T. Tanaka, Angew. Chem. Int. Ed. 2022, 61, e202200341; Angew. Chem. 2022, 134, e202200341], which has been published in final form at https://doi.org/10.1002/ange.202200341. This article may be used for non-commercial purposes in accordance with Wiley’s Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley’s version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and we ...
Dibenzodiazapyracylenes: Doubly N-Doped Cyclopenta-fused Polycyclic Molecules That Exhibit High Carrier Mobility


Abstract: Pyracylene is a unique cyclopenta-fused polycyclic aromatic hydrocarbon (CP-PAH) that exhibits dual aromatic characteristics. Herein we report the synthesis of doubly N-doped benzanallated pyracylenes, namely dibenzodiazapyracylenes, by oxidative N–N linking reaction of [2,2][2,5]pyrrolophen-type precursors. Dibenzodiazapyracylenes displayed well-ordered π-stacked molecular packing in the solid state, which were feasible for effective hole-transporting along the stacking direction. High carrier mobility was estimated by microwave conductivity measurements as compared to dibenzozulazine. The high HOMO level of dibenzodiazapyracylene was verified by electrochemistry and its persistent radical cation species has been detected.

Introduction

Cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) have been recognized as intriguing π-systems due to their unique resonance structure.[1] While the dominant resonance structure of CP-PAHs can be rationalized using the classical Clar’s sextet rule,[2] a minor yet conceivable conjugation effect appears when non-benzenoid carbocyclic conjugation circuit can be delineated. As the simplest motif, pyracylene (C3H3) (1) possesses a 10π conjugation circuit in the naphthalene segment (resonance structure 1A), while a 12π conjugation circuit can be also delineated along the periphery including the two pentagons (resonance structure 1B) (Figure 1).[3] A combined experimental and computational study concluded that 1 exhibited dual aromatic and antiaromatic characters from the structural and energetic point-of-views. Despite such an interesting entity, its structural modifications have been rarely explored. Murata et al. have recently reported tetracene-based extended pyracylene 2 and their unique reactivities.[4] Its organic field-effect transistor (OFET) performance has been investigated by Schneider et al., demonstrating an effective hole-transporting behaviour.[5] As another promising strategy, heteroatom-incorporation into PAHs has recently attracted significant attention and several functional heteroatom-doped PAHs have been utilized for electronic and optical applications.[6] However, only a few examples of sulfur-embedded pyracylenes have been reported, and their properties have not been well-exploited for materials applications.[7]

In this paper, we report the synthesis and properties of a doubly N-doped pyracylene analogue, namely dibenzodiazapyracylene (DBDAP). Dibenzopyracylene (DBP) is a benzanallated analogue of pyracylene having an essentially relevant electronic structure to 2, and DBDAP is a nitrogen embedded analogue of DBP having a hydrazine-type N–N segment replaced with an etheno C=C segment in DBP. Although DBP itself has never been prepared experimentally, the LUMO energy level has been calculated to be quite low (ca. −3.30 eV) as seen in many CP-PAHs that exhibited facile electron-accepting nature.[8] When two nitrogen atoms are embedded in the core of DBP, it becomes isoelectronic to the two-electron doped species...
of DBP, meaning that the HOMO of DBDAP derives from the LUMO of DBP. Thus, the HOMO of DBDAP lies at the higher level (ca. $-9.94$ eV), while the overall electronic structure remains to be CP-PAH-like because an annulene-type conjugation circuit like 1B still remains. By virtue of the smaller sized rigid structure which might be advantageous in making a solid-state structure feasible for carrier transporting, DBDAP would be a promising molecule for novel hole transporting materials. We herein report the successful synthesis of DBDAP by oxidative N–N linking reaction of [2.2](2,5)pyrrolophanes coupled product C shown a molecular ion peak at (Scheme 1) 1,2 by Suzuki phenyleneaza[8]circulenes, involving the possible contribution of the central 8π synthesized by fold S studied.

In addition, its OFET device applications and unique optical and redox properties will be studied.

Results and Discussion

Synthesis and structures of [2.2](2,5)pyrrolophanes

Recently, we have explored tetraaza[8]circulene 4a as a new class of planar nitrogen-doped PAHs, which can be synthesized by fold-type oxidation reaction of an orthophenylene-bridged cyclic tetrapyrrole 3a. In the series of heterocirculenes, the susceptible electronic properties involving the possible contribution of the central 8π cyclooctatetraene have been investigated from both experimental and theoretical viewpoints. Serendipitously, during our investigation on the synthesis of various substituted az[a]circulenes, we discovered a synthetic route toward obtaining novel doubly nitrogen-doped pyracyclenes. The orthophenylene-bridged cyclic tetrapyroles like 3a, is usually obtained by Suzuki-coupling reaction of $a,a'$-diborylated dipyrrole 7 with 1,2-dibromobenzene in a standard concentration (ca. 0.10 M). When we used 1,2-dibromo-4,5-difluorobenzene as a coupling partner and the reaction was run under high dilution (ca. 4.0 mM) in THF/H$_2$O, a different product 5b was obtained in 18% yield (Scheme 1). High-resolution atmospheric-pressure-chemical ionization time-of-flight (HR-APCI-TOF) mass spectrometry showed a molecular ion peak at $m/z = 318.0978$ (calcd. for C$_9$H$_7$F$_2$N$_2$: $m/z = 318.0963$), indicating that the product was a 1:1 coupled product; the compound was denoted as [2.2](2,5)pyrrolophane 5b. Under the same conditions, the reaction of 7 with 1,2-dibromobenzene furnished [2.2](2,5)pyrrolophane 5a in 25% yield. The $^1$H NMR spectrum of 5a in CDC$_3$ exhibits a signal at 6.35 ppm due to the pyrrolic $\beta$-protons, two signals at 7.33 and 7.56 ppm due to the phenylene protons, and a broad peak at 6.85 ppm due to the NH protons. The $^1$H NMR spectrum of 5b showed rather split signals due to the lower symmetry and presence of fluorine atoms, wherein the NH signal was observed at 6.82 ppm. The NH signals of 5a and 5b were up-field shifted as compared to those of 7, which can be attributed to the ring-current effect of the pyrrole unit on the other side. Single crystals of 5a and 5b were obtained by slow diffusion of $n$-hexane into their dichloromethane solutions. The structures were confirmed by X-ray diffraction (XRD) analysis (Figure 2). Two benzene units are located in the same plane and two pyrrole units in 5a and 5b are tilted with the dihedral angles between the benzene and pyrrole units of 57.8° and 54.2°, respectively. The two pyrrole units were slip-stacked in an anti-parallel manner and the mean distance between the pyrrole planes was 2.4 Å in both 5a and 5b.

The cyclic products 5a and 5b may serve as a precursor for dibenzodiazapyracylenes (hereafter, DBDAP is referred to as 6a or 6b to distinguish the substituents). The following oxidative N–N linking reaction will be described in the next section. Here, the structure of 5a itself would be of interest since it can be regarded as a smaller sized porphyrinoid, namely dibenzodiphyrin(2,2). However, it is a pale-yellow powder in the solid state and the porphyrin-like dye characters are not expected. Indeed, the absorption spectra of 5a and 5b show UV bands at ~300 nm and weak shoulder bands in the range of 320–400 nm (Figure 3). Interestingly, 5a shows green emission in the solid-state in the range of 400–700 nm with quantum yield (Ψ) of 0.14, while 5b exhibited a similar emission with much smaller efficiency ($\Phi$ = 0.023). In the crystal packing structure of 5a, molecules are p-stacked with NH protons pointing onto the benzo $\pi$-plane (Figure S7-1). Such NH–$\pi$ interactions and well-ordered molecular packing are not feasible in 5b (Figure S7-2). Since solvent molecules are not included in the crystals of 5a and 5b, similar packing structures are assumed in the powder states and the differences in the solid-state emission of 5a and 5b were attributed to the different packing structures.

Scheme 1. Concentration-dependent synthesis of cyclic tetrapyrrole 3a and 3b, and [2.2](2,5)pyrrolophanes 5a and 5b.
In addition, a new C–N bond formed between the pyrrolo nitrogen and the α-position of the other pyrrolo segment, giving rise to spiro-conjugated pyrrolo[2,1-α]isoindole structures (Figure 4).\(^{[16]}\) In addition, a new C–C bond formed between the other α-positions of two [2.2][2.5]pyrrolophane units in 8, with a slightly longer bond length (1.587(2) Å) than the typical one (1.53 Å). In contrast, a hydroxide is attached at the α-position of 9, which may derive from moisture in the air. In both 8 and 9, two sp\(^2\) carbons were detected in their \(^{13}\)C NMR spectra (Figures S3-14 and S3-16). Difluoro derivative 5b was also converted to 6b under the same conditions with a slightly lower yield (6%). The structures of 6a and 6b will be discussed later in detail.

**Oxidation reactions of [2.2][2.5]pyrrolophanes**

Next, we attempted oxidation reactions of 5a and 5b. In an initial experiment, 5a was treated with PbO\(_2\) in CH\(_2\)Cl\(_2\), which afforded white solids of 8 in 15% yield (Scheme 2). HR-APCI-TOF mass spectrometry showed a molecular ion peak of 8 at \(m/z = 562.2149\) (calcd. for C\(_{26}\)H\(_{25}\)N\(_7\): \(m/z = 562.2152\)), indicating a dimeric product. To suppress dimerization, mild oxidation conditions were considered, and we employed a base-promoted coupling under aerobic conditions, which has been used for the intramolecular NH–NH coupling of phenoxazine dimer\(^{[17]}\) and azaanthracene dimers.\(^{[18]}\) In the presence of 5 equivalents of potassium tert-butoxide in air, a solution of 5a in THF was stirred for 36 h. After separation, orange solids of 6a were obtained (13% yield) along with white solids of 9 (38% yield). HR-APCI-TOF showed molecular ion peaks of 6a and 9 at \(m/z = 280.1000\) (calcd. for C\(_{10}\)H\(_{7}\)N\(_2\): \(m/z = 280.1000\)) and \(m/z = 298.1101\) (calcd. for C\(_{10}\)H\(_{6}\)N\(_2\)O: \(m/z = 298.1101\)), respectively. This implies that 6a is the desired N–N linked product and that 9 was produced with the involvement of molecular oxygen or water. The \(^1\)H NMR spectral feature of 6a is consistent with its \(D_{∞h}\) symmetry (vide infra). The structures of 8 and 9 were finally revealed by XRD analysis, which showed that new N–C bonds formed between the pyrrolic nitrogen and the α-position of the other pyrrolo segment, giving rise to spiro-conjugated pyrrolo[2,1-α]isoindole structures (Figure 4).\(^{[19]}\) Spin-density profiles of 5a under oxidation conditions

To understand the reactivity of 5a for producing 6a, 8, and 9, cyclic voltammetry was conducted. In CHCl\(_3\) with 0.1 M n-Bu\(_4\)NPF\(_6\) as an electrolyte, 5a exhibits an irreversible oxidation peak at 0.40 V against ferrocene/ferrocenium ion couple. The oxidation peak of 5b is anodically shifted to 0.48 V due to the electron-withdrawing effect of the fluorine atoms. The irreversibility of the oxidation peaks implies the generation of the neutral radical species due to the release of the acidic NH proton in the radical cation state. Under basic conditions, the population of the neutral radical may increase and the spin-density is spread over the molecule. The calculated spin-density distribution of the neutral radical of 5a shows that the spin-density is highest at the α-position of the pyrrolo segment rather than at the nitrogen site, which is consistent with the high reactivity at the α-position (Figure S8-14). After forming the N–C bond, the radical intermediate was quenched by dimerization at the other α-positions or a reaction
with water to give 8 or 9, respectively. Notably, both 8 and 9 show blue emission in THF in the range of 370–500 nm with relatively large quantum yields (8: 0.48 and 9: 0.72) (Figures S5-1 and S5-2). The high fluorescence quantum yield of 9 might lead to the design for novel blue-emitting dyes as this kind of isoxindole derivatives have been utilized for light-emitting devices.\(^\text{[19]}\)

### NMR spectra and X-ray structures of 6a and 6b

The \(^1{H}\) NMR spectrum of 6a in benzene-\(d_6\) is shown in Figure 5a. A singlet is observed at 6.12 ppm which is ascribed to the pyrrole \(\beta\)-protons; in addition, two benzo-protons are observed at 6.98 and 6.72 ppm. These peaks are slightly, but distinctly, shielded as compared to those of 5a. This NMR spectral profile was independent of the temperature (see SI). To compare the NMR shielding effects, structurally relevant dibenzoullazine (Ulz) was prepared according to a previously reported method.\(^\text{[20]}\) The \(^1{H}\) NMR spectrum of Ulz in benzene-\(d_6\) is shown in Figure 5b. All the proton signals of Ulz appeared in the range of 7.1–8.1 ppm, thus confirming that the peaks in 6a are unusually shielded. The \(^1{H}\) NMR signals of 6b showed similar peak shifts (Figure S3-17). These results may indicate the involvement of 12\(\pi\) antiaromatic contribution in 6a and 6b, in addition to the aromatic contribution as seen in pyracylene (Figure 1a).

![Fig 5](https://example.com/fig5.jpg)

Figure 5. \(^1{H}\) NMR spectra of (a) 6a and (b) Ulz in benzene-\(d_6\) at room temperature.

The nuclear independent chemical shift (NICS)[\(^\text{[21]}\)] values were calculated with the GIAO method at the B3LYP/6-311G(d,p) level (Figure 6). In rings A and C, negative NICS values (NICS(0)/NICS(1))\(^\text{zz}\): \(-4.55/\sim 15.40\) and \(-13.95/\sim 25.34\) ppm, respectively) were calculated, while the values were positive at ring B (+7.32/+18.40 ppm). In the case of Ulz, the NICS values of rings A and C were more negative (NICS(0)/NICS(1))\(^\text{zz}\): \(-7.10/\sim 22.87\) and \(-15.84/\sim 35.41\) ppm, respectively) while the values at ring B were almost cancelled (+0.54/+1.33 ppm). In the case of DBP and 2, the NICS values are positive at the center of five-membered rings (Figure S8-9). These comparisons indicate the following facts: i) the paratropic ring current effect derived from the global annulenic resonance is stronger in the order DBP > 2 > 6a. ii) The lower order of 6a would be attributable to the predominant contribution of local aromaticity at the pyrrole segments. III) Still, to explain the difference in the NMR shift of Ulz, a weak yet decent contribution of antiaromatic resonance effect may be conceivable in 6a. Consistently, the ACID calculation visualized the localized aromatic ring-current flows in 6a as the dominant contribution of the resonance hybrid (Figure S8-12 and S8-13).

![Fig 6](https://example.com/fig6.jpg)

Figure 6. NICS(0) (top) and NICS(1)\(^\text{zz}\) (bottom, parenthesized) values of (a) 6a and (b) Ulz.

Single crystals of 6a and 6b were obtained by slow diffusion of \(n\)-hexane into their dichloromethane solutions (Figure 7).\(^\text{[15]}\) Both 6a and 6b show planar structures and their mean-plane deviation (MPD) values are calculated as 0.010 and 0.012 \(\AA\), respectively. The HOMA values are calculated at each ring, which again confirm the dominant contribution of local aromaticity (Figures S7-8 and S7-10). The N–N bond lengths (1.357(2) \(\AA\) for 6a and 1.354(2) \(\AA\) for 6b) are slightly shorter than the typical N–N bond length with the estimated bond-order of 1.038 (Figures S7-7 and S7-8). In the crystal packing structures, both 6a and 6b are packed with \(\pi\)–\(\pi\) distances of 3.295 and 3.359 \(\AA\) for 6a and 6b, respectively. The thermogravimetric analysis (TGA) revealed that the microcrystalline samples of 6a and 6b are stable up to 280–289 °C (5% mass loss) under a nitrogen atmosphere (Figures S10-1 and S10-2).

![Fig 7](https://example.com/fig7.jpg)

Figure 7. X-Ray crystal structures of (a) 6a and (b) 6b with thermal ellipsoids at a probability level of 50%.

### Optical properties in solution and in the solid-state
Figure 8 shows the UV-Vis absorption and fluorescence spectra of 6a and 6b. Compared with cyclophone 5a and 5b, 6a and 6b exhibit a sharp band at ~300 nm along with weak bands in the range of 350–400 nm. Besides, very weak absorption tail reaches 500 nm. No emission was detected in THF. These spectral features are supported by TD-DFT calculation at the level of B3LYP/6-311G(d,p). The forbidden HOMO–LUMO transition appears at 467 nm (f = 0.0000). However, 6a and 6b exhibit weak emission in the solid-state peaked at ~600 nm (Φr = 0.045 in 6a and Φr = 0.009 in 6b). To interpret the emission, diffuse reflectance spectra were measured, which showed identical peak wavelengths compared to those of the solution-state absorptions. Although both 6a and 6b are stacked with the interactive π–π distances in the crystal structure, the intermolecular interaction does not strongly affect the absorption profile. The fluorescence lifetimes were measured in the solid state by time-correlated photon-counting technique. The fluorescence decay profiles of 6a and 6b were fitted with three exponential decay profiles with fast decay component less than 1 ns, ns-order decay component (6.4 and 3.3 ns, respectively), and a small proportion of slow decay component (15.3 and 10.6 ns, respectively), which implied that a small component viable to adopt intermolecular interaction contributes to the solid-state emission.

Figure 8. UV-Vis absorption spectra in THF (solid black), diffuse reflectance spectra using the Kubelka-Munk function (solid blue), and solid-state fluorescence (dashed blue) spectra of (a) 6a and (b) 6b (excited at 300 nm in the solid state).

Charge transport properties

The well-ordered π-stacked packing structure of the compounds may show the feasibility of an organic semiconductor material with thermal fluctuation-tolerant 2D pathways for charge carriers. TRMC measurement was employed to determine charge carrier mobility under photo-injection of carriers into condensed phases. Figure 9a shows the kinetic traces of observed photoconductivity suggesting far higher conductivity in 6a than in Ulz. Photogenerated charge carriers confined in microcrystalline domains exhibit high stability over 100 μs regime (Figure 9b). The yield of photo carrier generation (Φpc) under an electric field allows us to estimate the maximum number of photogenerated charge carriers, and hence to calculate estimates of charge carrier mobility. Clear photo-current transients were observed for compounds 6a and 6b in the set of electrodes with 5 μm gap (Figure 9c). Derived values of Φpc were 9 × 10⁻⁴ and 2 × 10⁻³, respectively for 6a and Ulz at E = 0 by extrapolation of field dependence (Figure S13-2). Minimum charge carrier mobility in 6a of μ = 1.3 cm²/V·s is two orders of magnitude higher than that in Ulz (μ = 0.02 cm²/V·s⁻¹). DFT calculations were performed for charge transfer integrals (JAA) of holes and electrons with in-plane configuration of dimers AA and AB (Figure 10). The value of JAA in 6a was significantly higher than that in Ulz, reaching up to ~100 meV for holes; this is consistent with the observed high μ value in 6a. However, the most striking contrast was observed in the values of JAA(AB) and JAA(AA), suggesting the lack of two-dimensional pathways for charge carriers. OFET devices were fabricated for vacuum-deposited polycrystalline 6a with 50 μm source-drain ‘gaps’ in bottom-contact configurations which was only the choices due to high vacuum pressure of 6a under vacuo, reflecting its unique sublimation capability for the future dry processing. Clear gate voltage dependence was observed in the range of Vg = −50 V to +50 V (Figure 9d). The estimated hole mobility of 2.5×10⁻⁴ cm²/V·s⁻¹ was indeed less feasible as compared with those of 2 or tetracene[5,24] and further optimization of the device fabrication method will be necessary with regard to the layer thickness and domain morphology. Nevertheless, it has been proved that the design of dibenzodiazapyracylene is potentially suitable for OFET applications.

Figure 9. (a) Photoconductivity transients recorded in microcrystalline 6a (red) and Ulz (blue) upon excitation at 355 nm, 9.1 × 10⁻¹⁵ photons cm⁻². (b) Transient recorded in 6a for entire time range with logarithmic time scale. (c) Photo-current transients in 6a (blue-turquoise, E = 4–60 × 10⁻⁴ V cm⁻¹) and Ulz (orange-red, E = 4–60 × 10⁻⁴ V cm⁻¹) with comb-type electrode with a width of 2 mm and gap of 5 μm. (d) Source-drain current-voltage output characteristics of 6a depending on the gate voltages from 0 V (purple) to −50 V (red).
Chemical oxidation

The cyclic voltammetry showed reversible oxidation waves at 0.21 V for 6a and 0.40 V for Ulz against ferrocene/ferrocenium ion couple (Figure S1a and S9-5). The estimated HOMO energy levels are consistent with the DFT calculated ones (Figure S8-6). In addition, the second oxidation waves were observed at 0.72 V for 6a as a reversible peak. The oxidation waves of 6b were anodically shifted relative to those of 6a by 0.04-0.08 V (Figure S9-4). Relatively large gaps between the first and second oxidation potentials ($\Delta E_{ox} = 0.51$ V for 6a and 0.47 V for 6b) may be attributable to the large on-site Coulomb repulsion within the relatively small n-system or to the embedded hydrazine-type N-N segment. This situation leads to stabilization of the radical cation state of 6a. Indeed, upon addition of tris(4-bromophenyl)ammoniumyl hexachloroantimonate (Magic Blue) into a solution of 6a in CH2Cl2, clear spectral change was observed with identification of isosbestic points (Figure 11b). New peaks around 500 nm as well as NIR peaks in the range of 800-1200 nm appear until the addition of an equimolar amount of the oxidant. The radical cation was persistent under ambient conditions and further addition of the oxidant essentially gave no spectral changes. The solution was quantitatively recovered upon reduction by hydrazine. DFT calculation for the radical cation of 6a displays a well-delocalized spin-density distribution (Figure 11c). Similar to the radical of 5a, the pyrrolic Ï-positions have large coefficients rather than the nitrogen atoms, while the value is significantly smaller due to the effective spin-delocalization onto the whole n-surface. Although isolation of the radical cation as well as the generation of dications by more strong oxidants have not yet been successful, the rich redox behavior of 6a has been shown as an advantageous feature of nitrogen-doped PAHs to provide stable electronic conductive pathways for radical ions as charge carriers under ambient conditions as demonstrated in this work.

Conclusion

In conclusion, a novel class of nitrogen-doped CP-PAH, dibenzodiazapryracylene 6a,b, were successfully synthesized and characterized. By comparing their 1H NMR spectra and NICS values to those of reference compounds, a small yet decent contribution of 12m antiaromaticity in 6a,b has been shown, which differentiates them from usual polyyclic aromatic molecules. In addition, their condensed packing structures in the solid state allowed for hole transporting with high carrier mobility. Nitrogen-incorporation has been proved to be a particularly effective strategy to modulate the electronic states of CP-PAHs and chemically persistent radical cation of 6a has been characterized. By exploiting these concepts and outcomes, we are ongoing to create novel n-systems with an expectation for high-performance hole transporting materials.

Acknowledgements

The work was supported by JSPS KAKENHI Grant Numbers (JP20K05463 and JP21H05480). T.T. gratefully acknowledges the Foundation of the Promotion of Ion Engineering for financial support. The authors acknowledge Prof. Dr. H. Yorimitsu (Kyoto University) for HR-APCI-TOF MS measurements and Dr. S. Saito (Kyoto University) for TGA measurements.

Keywords: antiaromaticity • hole-transporting materials • microwave conductivity • polyacyclic aromatic hydrocarbons • solid-state emission


The definition of porphyrinoids is expressed as triphyrin (1.1.1) in which the numbers in the bracket indicates the number of meso-carbons. In this respect, 6a can be described as dibenzoporphyrin (2,2).

The same spectral change was observed by electrospectroscopy upon application of a voltage from 0 to 1.1 V (See Figure S11-1).

The definition of porphyrinoids is expressed as triphyrin (1.1.1) in which the numbers in the bracket indicates the number of meso-carbons. In this respect, 6a can be described as dibenzoporphyrin (2,2).

The same spectral change was observed by electrospectroscopy upon application of a voltage from 0 to 1.1 V (See Figure S11-1).
A novel nitrogen-doped CP-PAH, dibenzodiazapyracylene, was successfully synthesized and characterized. The aromatic and antiaromatic resonance hybrid characters have been verified by comparing their $^1$H NMR spectra to those of reference molecules. Their condensed packing structures in the solid state allowed for the effective hole transporting.