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# 5,11-Diazadibenzo[*hi*,*qr*]tetracene: Synthesis, Properties, and Reactivity toward Nucleophilic Reagents

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Abstract: 5,11-Diazadibenzo[hi,qr]tetracene was synthesized as a new nitrogen-substituted polycyclic heteroaromatic compound through Pd-catalyzed cycloisomerization of an alkyne precursor oxidative cyclization followed bv with bis(trifluoroacetoxy)iodobenzene. The substitution of imine-type nitrogen atoms significantly enhanced the electron-accepting character and facilitated the direct nucleophilic addition of arylamines under strongly basic conditions to afford the desired amino-substituted products. The introduction of amino groups induced a remarkable red-shift in their absorption spectra; the tetrasubstituted product exhibited intense near-infrared absorbing property. Furthermore, the  $\pi$ -electronic system, which includes a redox-active 1,4-diazabutadiene moiety, underwent reversible interconversion to its corresponding reduced form upon reduction with NaBH<sub>4</sub> and aerobic oxidation.

Polycyclic heteroaromatic molecules (PHAs) are an attractive class of organic functional chromophores and semiconductors owing to specific characteristics resulting from their substituted heteroatoms.<sup>[1]</sup> To date, a large number of PHAs have been developed for practical applications in organic electronics<sup>[2]</sup> as well as to obtain a deeper understanding of the physical properties of  $\pi$ -electronic systems.<sup>[3]</sup> The substituted nitrogen atoms in PHAs can be classified into amine- and imine-type atoms. The former usually make π-electronic systems electronrich,<sup>[4]</sup> while the latter exhibit highly electron-accepting characteristics.<sup>[5]</sup> In principle, these contrasting structures are interconvertible via redox reactions, which is accompanied by drastic changes in their electronic properties.<sup>[6]</sup> However, there limited reports on redox-switchable have been Nheteroacenes.<sup>[7]</sup> Osuka et al. reported a 1,5-naphthyridine-fused porphyrin dimer 1 possessing a redox-active 1,4-diazabutadiene linkage that is interconvertible with its reduced 1,2diaminoethene form (Figure 1a).<sup>[8]</sup> In this study, we designed a potentially redox-active PHA by replacing the porphyrin units in 1 with naphthalenes as more simplified aromatic skeletons (Figure 1b), which was named 5,11-diazadibenzo[hi,qr]tetracene (2),[9] adopting tetracene as the main core. The redox-active 1,4diazabutadiene structure has also been observed in a natural redox-active coenzyme of flavin adenine dinucleotide (FAD, Figure 1c), suggesting the reversibility of this interconversion and its applicability to artificial oxidation catalysts.<sup>[10]</sup> From another perspective, compound **2** can be regarded as a nitrogen-substituted zethrene derivative, which exhibits unique optical, electronic, and magnetic properties.<sup>[11]</sup> Recently, Wu et al. developed nitrogen-substituted heptazethrene **3a** and octazethrene **3b** by oxidation of their corresponding dihydroprecursors **4a** and **4b**, respectively, as open-shell diradicaloids being unstable under ambient conditions (Figure 1d).<sup>[12]</sup> In this study, we report the synthesis, characterization, and reactivity of 5,11-diazadibenzo[*hi*,*qr*]tetracene **(2)** toward nucleophilic reagents.



**Figure 1.** Structures of (a) redox-active porphyrin dimers **1** and **1'**, (b) 5,11diazadibenzo[*hi*,*qr*]tetracene (**2**), (c) natural FAD and FADH<sub>2</sub>, and (d) nitrogensubstituted zethrene derivatives **3a** and **3b**.



**Scheme 1.** Synthesis of 5,11-diazadibenzo[*hi,qr*]tetracene **(2)**. Reaction conditions: (a) trimethylsilylacetylene, Pd(PPh<sub>3</sub>)Cl<sub>2</sub>, Cul, NEt<sub>3</sub>, 50 °C, 95%; (b) KF, MeOH, 40 °C, 99%; (c) **5**, Pd(PPh<sub>3</sub>)Cl<sub>2</sub>, Cul, NEt<sub>3</sub>, 50 °C, 72%, (d) PdCl<sub>2</sub>, THF, 60 °C, 86%; (e) PIFA, CH<sub>2</sub>Cl<sub>2</sub>, RT, 52%.

The synthesis of 5,11-diazadibenzo[hi,gr]tetracene (2) is depicted in Scheme 1. The starting compound, 8bromonaphthalen-1-amine (5), was prepared from 1,8diaminonaphthalene, according to a literature procedure.<sup>[13]</sup> Bromide 5 was converted into terminal alkyne 6 using a Sonogashira coupling reaction with trimethylsilylacetylene, followed by desilylation of 6 using KF in MeOH solution in high vield. The Sonogashira coupling reaction of bromide 5 and acetylene 7 provided symmetrical alkyne precursor 8 bearing two amino groups in 72% yield. In the presence of a catalytic amount of PdCl<sub>2</sub>, alkyne 8 underwent a highly selective 6-endo cvclization to give cvclized product 9 in 86% vield. In the final step, we attempted the oxidative cyclization of 9. After screening a variety of oxidants in the reaction, the use of bis(trifluoroacetoxy)iodobenzene (PIFA) gave the best result, affording product 2 in 52% yield. In the <sup>1</sup>H NMR spectrum of 2, the disappearance of the NH signals and downfield-shifted aromatic signals ( $\delta$  8.9–7.6 ppm) supported the formation of product 2. In spite of its planar structure without any solubilizing substituents, compound 2 exhibited a certain degree of solubility in organic solvents, such as CHCl<sub>3</sub> (4.1 mg/mL) and tetrahydrofuran (THF, 2.5 mg/mL). The core structure of 2 was elucidated using X-ray crystallography after chemical modification (vide infra), although we failed to obtain single crystals of 2 suitable for analysis.



Figure 2. <sup>1</sup>H NMR spectra of 9 in (a) DMSO- $d_6$  and (b) CDCl<sub>3</sub> and (c) tautomerization between enamine form and imine form.

In our synthetic study, we observed the enamine-imine tautomerization of the 1H-benzo[de]quinoline fragment in intermediate 9 (Figure 2). The <sup>1</sup>H NMR spectrum of 9 recorded in dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) showed two NH (H<sup>a</sup> and H<sup>b</sup>) signals at  $\delta$  9.75 and 5.57 ppm with an integral ratio of 1:2 and one singlet corresponding to a vinyl-proton (H<sub>c</sub>) at  $\delta$  5.63 ppm (Figure 2a). In contrast, the <sup>1</sup>H NMR spectrum of **9** recorded in CDCl<sub>3</sub> appeared to be a mixture of two chemical species in a ratio of 1:0.3 (Figure 2b). The major component showed the same spectral pattern as that observed in DMSO- $d_6$  consisting of two NH (H<sup>a</sup> and H<sup>b</sup>) signals at  $\delta$  6.46 and 4.79 ppm in a 1:2 ratio and a vinyl-proton (H<sub>c</sub>) at  $\delta$  5.76 ppm. The minor component showed two characteristic doublets at  $\delta$  3.81 and 3.37 ppm with a large coupling constant of 15.6 Hz. These doublets can be assigned to a methylene group ( $H_d$  and  $H_e$ ), which causes geminal coupling. Thus, the minor component was characterized as the imine form generated via imine-enamine tautomerization (Figure 2c). The observed solvent effect can be interpreted in terms of hydrogen bonding interactions. In DMSO $d_6$ , the enamine form was stabilized by hydrogen bonding between the NH proton and DMSO- $d_6$ , and observed as the sole species. In contrast, CDCl<sub>3</sub> acts as a hydrogen bonding donor to stabilize the basic imine form to make the observable species, while density functional theory (DFT) calculation results indicated that the enamine form was more stable than the imine form by 20.4 kJ/mol (Figure S16). This is the first observation of enamine-imine tautomerization in the 1*H*-benzo[*de*]quinoline  $\pi$ system despite the existence of several studies reporting the synthesis of analogous compounds.[14]

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Scheme 2. Direct amination of 2. Reaction conditions: (a) 4-*tert*-butylaniline, NaH, DMF, RT, 52%; (b) diphenylamine, NaH, DMF, RT, 26%.

To elucidate the core structure of 2 using X-ray crystallography, we attempted the chemical transformation of 2 into derivatives with higher crystallinity. We serendipitously found that compound 2 underwent direct amination with arylamines under strongly basic conditions (Scheme 2). Treatment of 2 with 4-tertbutylaniline and NaH in N,N-dimethylformamide (DMF) gave compound **10** as the major product, in which one hydrogen atom was substituted by 4-tert-butylaniline at position a. On the other hand, the use of diphenylamine instead of 4-tert-butylaniline furnished tetrasubstituted product 11, where the diphenylamino groups were installed at positions *b* and *c* in 26% yield. Although the detailed reaction mechanism is unclear, the reaction can be classified as an oxidative nucleophilic substitution of hydrogen,<sup>[15]</sup> which consists of the nucleophilic addition of the deprotonated amine to 2, followed by aerobic oxidation of the  $\sigma_H$ -adduct intermediate. A plausible reaction mechanism is shown in the Supporting Information (Scheme S1). The success of the reaction can be ascribed to the high electrophilicity of compound 2 and the high air sensitivity of the intermediate. Here, the reactions with 4-tert-butylaniline and diphenylamine provided different results in terms of the regioselectivity and number of amino groups introduced during the reaction. These differences can be explained by the presence of the second N-H bond in the arylamines studied. Namely, intramolecular hydrogen bonding stabilizes  $\sigma_{H}$ -adduct **A** (Scheme 2), forming a sixmembered ring structure to facilitate regioselective addition at position a. Moreover, product 10 is deprotonated under basic reaction conditions and the resulting anionic substituent in 10' strongly deactivates the  $\pi$ -electronic system toward the additional nucleophile.

X-ray crystallographic analysis of **10** and **11** unambiguously revealed the core structure of the diazadibenzotetracene and the regioselectivity of the direct amination reaction (Figure 3). In the crystal structure of **11**, the fused six-membered rings display

distinct bond alternations. The clearly shorter N–C2 bonds (1.3139(16) Å) compared to the N–C1 bond (1.3751(15) Å) indicate the localization of the double bonds at the N–C1 bond. Moreover, the single bond character of the C2–C2' (1.458(2) Å) and C2–C3 (1.4613(16) Å) bonds also supported the 1,4-diazabutadiene-type resonance structure. The dihedral angles between the  $\pi$ -systems and the amino groups (1.3° for **10** and 45.9–58.9° for **11**) suggest significant electronic interactions between these components. In the crystal packing structure, mono-aminated compound **10** forms a one-dimensional columnar structure via significant  $\pi$ - $\pi$  interactions with interplane distances of 3.34 and 3.36 Å, respectively (Figure S19). On the other hand, each  $\pi$ -system of tetraaminated **11** was spatially separated by the peripheral diphenylamino groups and solvent molecules (Figure S20).



Figure 3. X-Ray crystallographic structures, selected bond lengths, and selected dihedral angles of (a) 10 and (b) 11. The thermal ellipsoids showed 50% probability level. All hydrogen atoms except for NH and solvent molecules were omitted for clarity. Deposition numbers 2067726 (for 10) and 2067727 (for 11) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.



Figure 4. UV/Vis/NIR absorption (solid) and fluorescence (dashed) spectra of 2 (red), 10 (violet), and 11 (blue) in CHCl\_3.

Table 1. Summary of photophysical properties<sup>[a]</sup> and redox potentials<sup>[b]</sup> of 2, 10, and 11.

Compound	λ <sub>abs</sub> [nm]	λ <sub>em</sub> [nm]	Stokes shift [cm <sup>-1</sup> ]	$\Phi_{F}$	τ [ns]	<i>k</i> <sub>r</sub> [ns <sup>-1</sup> ]	<i>k</i> nr [ns⁻¹]	E <sub>red</sub> [V]	E <sub>ox</sub> [V]
2	568	585	512	0.10	5.98	0.0167	0.150	-1.33	-
10	635	-	-	-	-	-	-	-1.62	0.35

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#### **11** 798 - - - - - - - - - - - - - - - - 1.44 - 0.11

[a] In CHCl<sub>3</sub>. [b] In THF, versus ferrocene/ferrocenium.

The UV/vis/NIR absorption and fluorescence spectra obtained for 2, 10, and 11 are shown in Figure 4 and photophysical properties were summarized in Table 1. Compound 2 exhibits absorption peaks at 568 and 528 nm and a fluorescence peak at 585 nm. The distinct vibronic structure and small Stokes shift (512 cm<sup>-1</sup>) are typical of rigid aromatic  $\pi$ -electronic systems. The fluorescence quantum yield ( $\Phi_{\rm F}$ ) and fluorescence lifetime  $(\tau)$  were determined to be 0.10 and 5.98 ns. Using these values, the radiative  $(k_r)$  and non-radiative  $(k_{nr})$  deactivation rate constants were calculated to be 0.0167 and 0.150  $\ensuremath{\,\mathrm{ns}^{-1}}$  , respectively. When compared to unsubstituted compound 2, amine-adducts 10 and 11 exhibit drastically red-shifted absorption peaks at 635 and 798 nm, respectively. Compound 10 and 11 was not emissive probably because the low excitation energy facilitated the non-radiative deactivation. In particular, compound 11 shows intense NIR-absorbing property with a large molar extinction coefficient of 7.7  $\times$   $10^4\,M^{-1}\,cm^{-1}$  at 798 nm. The small solvent dependence of the absorption spectra (Figure S22) indicate the small charge transfer character between the electron-accepting diazatetracene core and electron-donating amino substituents.

The electrochemical properties of 2, 10, and 11 were investigated using cyclic voltammetry (CV) in THF utilizing the ferrocene/ferrocenium redox couple as a potential standard (Table 1, Figure S23). Diazadibenzotetracene 2 exhibits reversible reduction waves at -1.33 and -1.82 V, respectively. The first reduction potential was positively shifted by 0.46 V when compared to that of zethrene (-1.79 V),<sup>[16]</sup> the all carbon counterpart of 2, due to the incorporation of the electronaccepting nitrogen atoms. Moreover, the first reduction potential was slightly lower than that of conventional n-type organic semiconductors, such as fullerene derivatives (ca. 1.1 V) and perylene diimide derivatives (ca. 1.2 V), suggesting the potential utility of 2 as an electron-accepting material. Electrochemical studies on aminated compounds 10 and 11 also revealed the significant substitution effect of the amino groups. The reduction potentials of 10 (-1.62 V) and 11 (-1.44 V) were negatively shifted from that of 2, and the oxidation waves were observed at 0.35 V for 10 and -0.11 V for 11. DFT calculations on 2, 10, and 11 also revealed that the HOMO-LUMO levels were significantly perturbed by the amino groups, which is consistent with our electrochemical studies (Figure S17). The highly electrondonating character of 11 was ascribed to the delocalization of the HOMO over the whole molecule via antibonding interactions between the diazadibenzotetracene core and diphenylamino groups.



Figure 5. (a) Redox interconversion of 2 and changes in (b) solution color, (c) UV/Vis absorption, and (d) fluorescence spectra. Reaction conditions: (i) NaBH<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, RT; (ii) air, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, RT.

In the final stage of this study, we investigated the redox interconversion of 2. Compound 2 can be regarded as an oxidized form possessing a redox-active 1,4-diazabutadiene structure, which is interconvertible with its reduced 1,2diaminoethene structure 12 (Figure 5a). Upon the addition of an excess amount of NaBH<sub>4</sub>, the red solution of 2 turned into an orange solution under a nitrogen atmosphere in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (Figure 5b). However, the reduced orange dye immediately returned to 2 upon the addition of air-saturated water and was difficult to isolate in air. Thus, we attempted to observe the reduced species by monitoring the changes in the absorption and fluorescence spectra under a nitrogen atmosphere (Figure 5c,d). After the reduction step, the absorption peaks of 2 at 563 and 526 nm completely disappeared and new peaks emerged at 546, 507, 473, 426, and 401 nm. In the fluorescence spectra, an intense peak was observed at 562 nm. The spectra obtained for the reduced species were unchanged for 1 h, indicating sufficient stability under a nitrogen atmosphere. Exposure of the solution to air for 20 min resulted in the complete recovery of the absorption and fluorescence spectra observed for 2. These results indicate that compound 2 is a redox-active dye that undergoes a fully reversible interconversion between the highly air-sensitive reduced form. Although the molecular structure of the reduced form was not clearly confirmed, time-dependent density functional theory calculations provided a simulated UV/vis spectrum similar to the observed spectra and supported the formation of the corresponding the 1,2-diaminoethene structure 12 (Figure S18). Furthermore, <sup>1</sup>H NMR spectrum of 2 after the addition of NaBH<sub>4</sub> indicated that compound 2 underwent quantitative transformation into the reduced form whose spectral pattern is consistent with 12 (Figure S24). We

also attempted a similar redox interconversion of compound **10** and **11**, but no reaction was confirmed.

5,11-diazadibenzo[hi,qr]tetracene (2) In summary, was synthesized as a new nitrogen-substituted PHA bearing a redoxactive 1,4-diazabutadiene structure. Due to the substitution of imine-type nitrogen atoms, compound 2 showed enhanced electron-accepting character comparable to that of conventional n-type materials and specific reactivity toward nucleophilic reagents. The oxidative nucleophilic substitution of hydrogen with arylamines induced a remarkable change in the electronic properties resulting in the aminated products 10 and 11. Furthermore, compound 2 undergoes reversible interconversion into its reduced form upon reduction with NaBH<sub>4</sub>, followed by aerobic oxidation. Further investigations on potential applications of diazadibenzo[hi,qr]tetracenes as n-type materials or redox-active dyes are currently in progress in our laboratory.

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#### Entry for the Table of Contents



5,11-Diazadibenzo[*hi*,*qr*]tetracene was synthesized as a new nitrogen-substituted polycyclic heteroaromatic molecule. This compound showed enhanced electron-accepting character and specific reactivities toward nucleophilic reagents. The reaction with arylamines provided the aminated product that shows an intensely NIR-absorbing character. Furthermore, a reversible interconversion into the corresponding reduced form was realized.