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Highly Electron-Deficient Hexaazapentacenes and Their Dihydro Precursors

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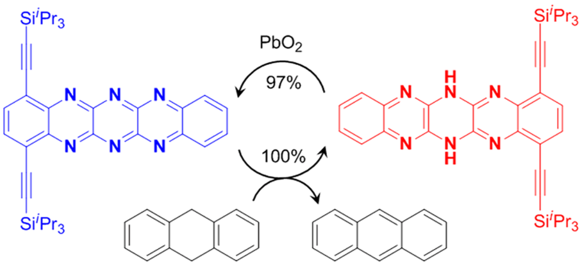
ABSTRACT



Novel silylethynylated *N*-heteropentacenes that have three adjacent pyrazine rings at the center of a pentacene backbone are reported. These hexaazapentacenes exhibit a record low energy level of lowest unoccupied molecular orbital (LUMO) for *N*-heteropentacenes and thus are able to oxidize dihydroanthracene to anthracene. Their synthetic precursors are the corresponding dihydrohexaazapentacenes, which exhibit interesting H-bonding.

N-Heteropentacenes, following their parent hydrocarbon, pentacene, have recently arisen as a new family of organic semiconductors exhibiting high performance in organic field effect transistors (OFETs).[1] *N*-Heteropentacenes have their properties, including solubility, electronic structures, molecular packing and semiconductor properties, highly dependent on the pattern of N atoms, which is defined by the number, position, and valence state of N atoms in the pentacene backbone.[2,3] Unprecedented patterns of N atoms therefore have good opportunities leading to new findings on *N*-heteropentacenes.[3,4] Here we report novel silylethynylated *N*-heteropentacenes (**1a**–**c**) that have three adjacent pyrazine rings at the center of the pentacene backbone as shown in Figure 1. Unlike the long-known fluorubine[5] and recently reported *N*-substituted fluorubines,[6] these hexaazapentacenes have six unsaturated

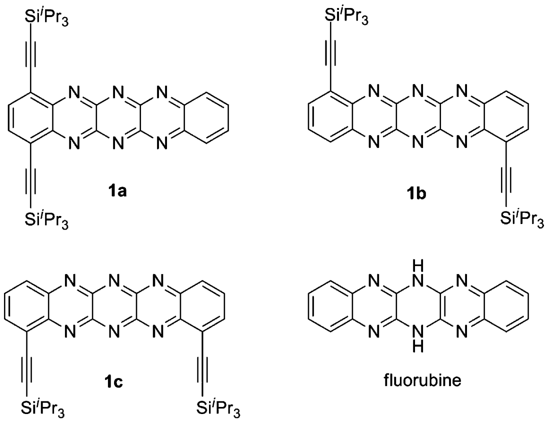


Figure 1. Structures of silylethynylated hexaazapentacenes (**1a**–**c**) and fluorubine.

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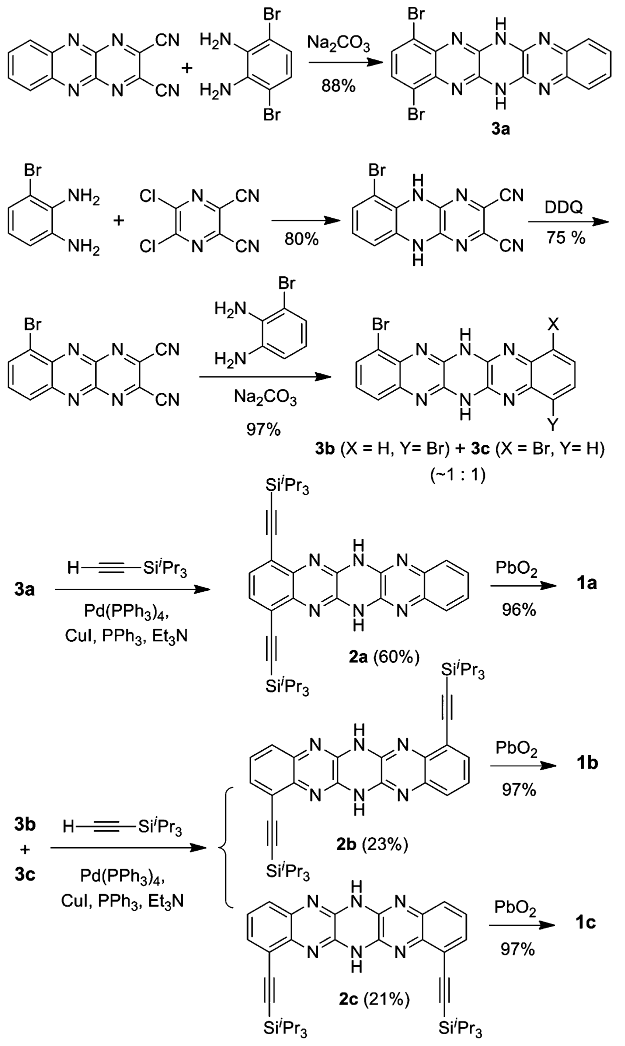
Scheme 1. Synthesis of **1a**−**c**



N atoms. With this unprecedented pattern of N atoms, **1a**−**c** are found to exhibit a record low energy level of lowest unoccupied molecular orbital (LUMO) for *N*-heteropentacenes and able to oxidize dihydroanthracene to anthracene. The synthetic precursors of **1a**−**c** are the corresponding dihydrohexaazapentacenes **2a**−**c** (shown in Scheme 1), which exhibit interesting H-bonding that is not observed from fluorubine or *N*-substituted fluorubines.

Shown in Scheme 1 is the synthesis of **1a**−**c**, which started with the construction of the dihydro-hexaazapentacene backbone by nucleophilic substitutions on the pyrazine rings.[7] Two isomers of dibromodihydrohexaazapentacene, **3b** and **3c**, were obtained as a nearly 1:1 mixture that was used in the next step without separation due to their low solubility. Sonogashira reactions of **3a**−**c** with triisopropylsilylacetylene resulted in dihydrohexaazapentacenes **2a**−**c**, and **2b** and **2c** were separated conveniently using column chromatography on silica gel. It is worth noting that this Sonogashira reaction required relatively high temperature (higher than 120 °C) and long reaction time (at least 48 h) because of the poor solubility and low reactivity of **3a**−**c**. Unlike most of the reported silylethynylated dihydro-*N*-heteropentacenes,[8] **2a**−**c** are resistant to oxidation by MnO_2[8] as well as O_2 in air,[9] DDQ, and pyridinium chlorochromate (PCC). PbO_2 was finally found effective to oxidize **2a**−**c** to the corresponding hexaazapentacenes (**1a**−**c**) almost quantitatively. Similar to the previously reported silylethynylated hexaazahexacene,[10] **1a**−**c** changed gradually back to **2a**−**c**, respectively, when their solutions or solids were stored in air under ambient light for several days. However, the mechanism for this reaction remains obscure.

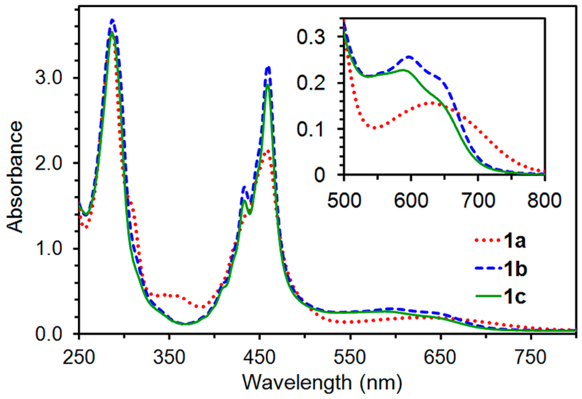


Figure 2. UV−vis absorption spectra of **1a**−**c** in CH_2Cl_2 (5×10^{-5} M).

Hexaazapentacenes **1a**−**c** form green solutions while dihydrohexazapentacenes **2a**−**c** form yellow solutions with strong green fluorescence. In comparison to the reported tetraazapentacenes that have two silylethynyl groups attached to the internal rings,[3,8] **1a**, **1b**, and **1c** exhibit blue-shifted, weaker and broader longest wavelength absorptions at 630 nm, 597 and 588 nm, respectively, as shown in Figure 2. The cyclic voltammograms of **1a**−**c** (shown in the Supporting Information) exhibit two reversible one-electron reduction waves in the testing window. The first half-wave reduction potential vs ferrocenium/ferrocene is −0.26 V for **1a**, −0.23 V for **1b**, and −0.29 V for **1c**, from which the LUMO energy levels of **1a**−**c** are estimated as −4.54 eV, −4.57 and −4.51 eV, respectively.[11]

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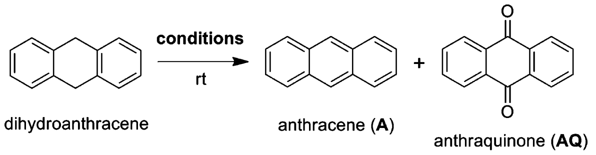
Compounds **1a**–**c** have lower LUMO energy levels than the reported silylethynylated monoazapentacene, diazapentacenes[12] and tetraazapentacenes[3,8] that do not have extra substituents. In particular, **1b** has the lowest LUMO energy level among all the known *N*-heteroacenes including those that have extra electron-withdrawing substituents, such as fluorine and nitro groups.[13] The record low LUMO energy levels of **1a**–**c** are in agreement with the earlier conclusion that the LUMO energy level of *N*-heteropentacene goes down with the increasing number of unsaturated N atoms,[2] particularly in the internal rings of pentacene.[3] From the optical gap and LUMO energy level, the energy level of highest occupied molecular orbital (HOMO) was estimated as −6.14 eV for **1a**, −6.33 eV for **1b** and −6.28 eV for **1c**. The very close LUMO energy levels and slightly different HOMO energy levels of **1a**–**c** suggest that C–C triple bonds have different contributions to the HOMO and LUMO. This is in agreement with the calculated HOMOs, which are delocalized to C–C triple bonds, and the calculated LUMOs, which are almost localized on the hexaazapentacene backbone.[14] On the other hand, the cyclic voltammograms of **2a**–**c** (shown in the Supporting Information) are very similar, exhibiting one quasi-reversible oxidation wave and one irreversible reduction wave at ca. 0.8 and −1.5 V vs ferrocenium/ferrocene, respectively. From these potentials, the HOMO and LUMO energy levels of **2a**–**c** were estimated as ca. −5.6 and −3.3 eV, respectively.[11]

The low LUMO energy levels of **1a**–**c** suggest that they may function as n-type semiconductors although the instability in the solid state limits their potential applications.[15] However, our attempts of fabricating thin film transistors of **1a**–**c** appeared unsuccessful because these compounds decomposed during thermal evaporation and formed disordered films with poor morphology during solution-based process. On the other hand, the relatively high LUMO energy levels and relatively low HOMO energy levels of **2a**–**c** suggest that these compounds are not suitable candidates for either n-type or p-type semiconductors.

The very low LUMO energy levels suggest that **1a**–**c** can function as oxidants in organic reactions. To test the oxidizing ability of these hexaazapentacenes, **1a** was selected as a representative to oxidize dihydroanthracene in both stoichiometric and catalytic reactions. As shown in Table 1 (entry 2), dihydroanthracene was completely oxidized by 1 equiv of **1a** to anthracene after 16 h. Because the reduction product of **1a** in this reaction is **2a**, which can be oxidized back to **1a** by PbO$_2$, it is possible to oxidize dihydroanthracene with **1a** in a catalytic manner with PbO$_2$ as the second oxidant. When 0.3 equiv of **1a** and 30 equiv of PbO$_2$ were used as the oxidant, dihydroanthracene was oxidized to anthracene in a yield of 89% as shown in Table 2 (entry 4). In control experiments, PbO$_2$ itself oxidized dihydroanthracene slowly to not only anthracene but also anthraquinone, which was, however, not observed from the crude products of the reactions using **1a** as the oxidant. The mechanism for this dehydrogenation reaction by **1a** presumably involves a transfer of hydride or a hydrogen atom from the benzyl group to the pyrazine nitrogen as suggested by its two reversible one-electron reductions.

Table 1. Oxidation of 9,10-Dihydroanthracene by **1a** and PbO$_2$



entry	conditions[a]	products[b] A (%)	products[b] AQ (%)
1	**1a** (1 equiv), 2 h	55	0
2	**1a** (1 equiv), 16 h	100	0
3	**1a** (0.3 equiv), PbO$_2$ (30 equiv), 2 h	22	0
4	**1a** (0.3 equiv), PbO$_2$ (30 equiv), 29 h	89	0
5	PbO$_2$ (30 equiv), 16 h	6	3
6	PbO$_2$ (30 equiv), 29 h	14	13

[a] The reactions were carried out in CDCl$_3$ at room temperature. [b] The yield was determined by ^{1}H NMR.

With adjacent pyrazine and dihydropyrazine rings that are not shielded by the bulky triisopropylsilyl groups, molecules of **2a**–**c** can in principle form intermolecular hydrogen bonds with each other. To study such hydrogen bonds, single crystals of **2a** and **2b** were grown from solutions in ethyl acetate and subjected to X-ray crystallographic analysis. Shown in Figure 3a is the crystal structure of **2a**, which exhibits a one-dimensional face-to-face π-stacking with head-to-tail arrangement. It is found that neighboring molecules of **2a** stack with each other with two slightly different arrangements alternating in one stack. One arrangement has the two π-faces separated by 3.35 Å and the two silicon atoms of neighboring molecules separated by 7.42 Å. In comparison, the other arrangement has two π-faces separated by 3.26 Å and the two silicon atoms of neighboring molecules separated by 13.75 Å, which is accompanied with a shift along the long axis of pentacene backbone. Intermolecular hydrogen bonds are not observed between the π-stacks of **2a** since the N–H moiety of each molecule of **2a** is somehow blocked by the triisopropyl groups of neighboring molecule in the same stack. Unlike its isomer **2a**, **2b** exhibits intermolecular hydrogen bonds but lacks π–π interactions in its crystal structure. As shown in Figure 3b, molecules of **2b** form a hydrogen-bonded ribbon, which has a shape of "X" as viewed along the

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(13) For the structures and energy levels of these silylethynylated N-heteropentacenes as well as the references, see the Supporting Information.

(14) The frontier molecular orbitals of **1a**–**c** and **2a**–**c** were calculated with the Gaussian 09 software package using simplified model molecules, which have smaller trimethylsilyl groups replacing the triisopropylsilyl groups. The geometries of these model molecules were first optimized at the B3LYP level of density functional theory (DFT) with the 6-31G(d, p) basis set, and the HOMO and LUMO were then calculated with the 6-311++G(d, p) basis set.

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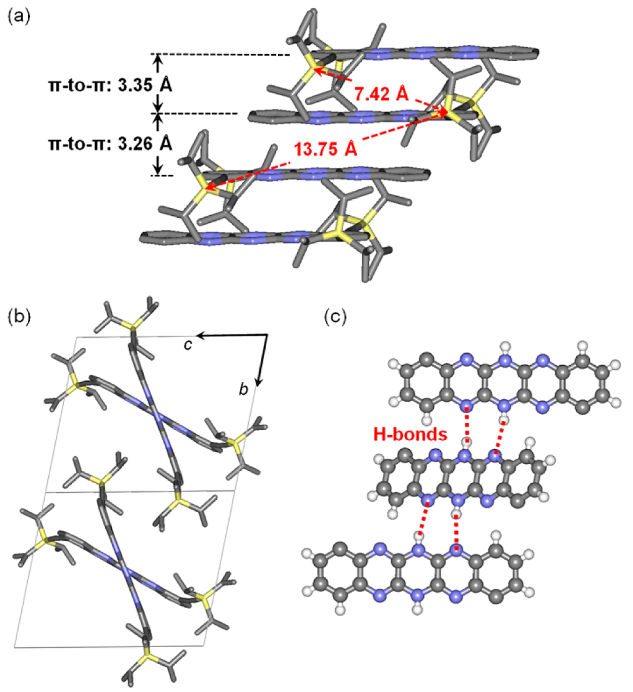

Figure 3. (a) Crystal structure of **2a** showing π-stacking; (b) crystal structure of **2b** view along the *a* axis of its unit cell; (c) hydrogen bonds between molecules of **2b** in the crystal structure. (Carbon, nitrogen, hydrogen, and silicon atoms are shown in gray, blue, white, and light yellow, respectively. For clarity, hydrogen atoms are removed in parts a and b and triisopropylsilylethynyl groups are removed in part c).

a axis of the unit cell. The double hydrogen bonds between molecules of **2b** as shown in Figure 3c have the N-to-N distances of 3.06 Å and 3.11 Å, the H-to-N distances of 2.27 Å and 2.29 Å, and the N−H−N angles of 152.5° and 159.2°. The N-to-N and H-to-N distances for the hydrogen bonds of **2b** are slightly larger than those found for the hydrogen bonds of unsubstituted dihydrotetraazapentacene[4] possibly due to the steric hindrance of bulky triisopropylsilyl groups.

Although the crystal structure of **2c** was not available as evidence for hydrogen bonds due to the difficulty in crystallizing **2c**, intermolecular hydrogen bonds of **2c** were found in solution with ^{1}H NMR spectroscopy. Among the two active protons of **2c**, only one is available for intermolecular hydrogen bonds, while the other is shielded by the two bulky triisopropylsilyl groups. As shown in Figure 4, when a solution of **2c** in $CDCl_3$ (2 mol/L) is cooled from 22 to −40 °C, the broad peak for exposed N−H (highlighted in magenta) exhibits a significant downfield shift of 2.1 ppm, while the signal of shielded N−H (highlighted in green) only shifts to downfield by less than 0.2 ppm. This indicates formation of intermolecular hydrogen bonds,[16] which is accompanied with less dynamic molecules at lower temperature. Although the low solubility of **2c** in

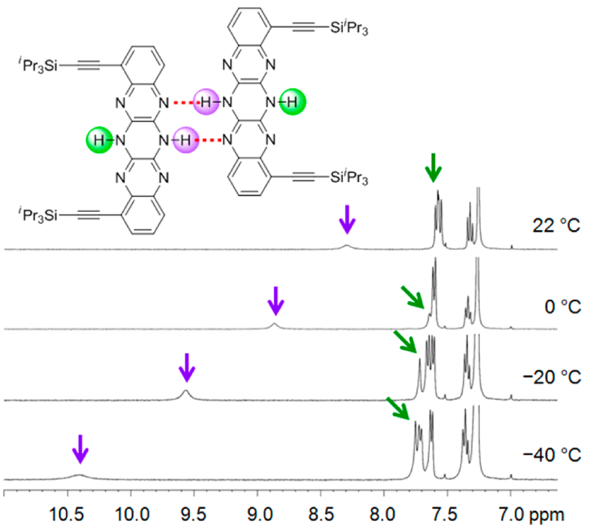

Figure 4. H-bonded dimer of **2c** and selected ^{1}H NMR spectra of **2c** when cooled from 22 to −40 °C.

non-H-bonding solvents prevented varying its concentration by a large degree, when a solution of **2c** in $CDCl_3$ increased its concentration from 0.3 to 2 mmol/L, the broad peak for exposed N−H exhibited a downfield shift of 0.5 ppm as shown in the Supporting Information.

In summary, three highly electron-deficient silylethynylated hexaazapentacenes (**1a**−**c**) with an unprecedented pattern of N-atoms and their dihydro precursors (**2a**−**c**) are reported. These hexaazapentacenes (**1a**−**c**) are found to exhibit LUMO energy levels lower than −4.50 eV and thus able to oxidize dihydroanthracene to anthracene in both stoichiometric and catalytic reactions. Among the three isomeric dihydrohexaazapentacenes, **2b** exhibits hydrogen bonding in crystals and **2c** exhibits hydrogen bonding in solution. In contrast, the crystal structure of **2a** lacks hydrogen bonding but is dominated by π-stacking possibly in relation to the arrangement of bulky substituents. The instability of hexaazapentacenes **1a**−**c** in ambient conditions suggests a maximum number of five unsaturated nitrogen atoms for *N*-heteropentacenes to be stable n-type organic semiconductors.

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Supporting Information Available. Details of synthesis, cyclic voltammetry, UV−vis absorption, DFT calculation, NMR spectra, and CIF for **2a** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.