Organic Semiconductors

Extension of N-Heteroacenes through a Four-Membered Ring

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Abstract: The synthesis of novel π -extended N-heteroacenes, which have a large tetraazaacene subunit and a quinoxaline subunit connected through a four-membered ring, is reported. They were studied with experimental and computational methods in comparison to the corresponding tetraazaacenes. As found from the DFT calculation, the fourmembered ring is a better linker than a five-membered ring

Introduction

N-heteroacenes have recently received considerable attention with respect to synthesis, property evaluation, and applications.^[1,2] Most of the known N-heteroacenes are N-heteropentacenes,^[3] which are an important class of organic semiconductors exhibiting high performance in organic thin film transistors (OTFTs).^[4,5] Similar to acenes,^[6] N-heteroacenes become less stable and less soluble as their length increases. As a result, N-heteroacenes larger than N-heteropentacenes are rare, and the largest fully characterized N-heteroacene so far is a diazaheptacene that was protected by four bulky tri(sec-butyl)silyl groups from fast dimerization.^[2] This becomes an obstacle to development of organic semiconductors based on larger N-heteroacenes, which can in principle have more extensive electron delocalization and greater intermolecular $\pi\text{-}\pi$ overlap in the solid state. Here we demonstrate that N-heteroacenes can be extended through a four-membered ring into linear polycyclic frameworks with up to eight fused rings. As shown in Figure 1a, novel π -extended N-heteroacenes **1a** and 1b have a four-membered ring connecting a large tetraazaacene (tetraazatetracene 2a and tetraazapentacene 2b, respectively) with quinoxaline, one of the smallest N-heteroacenes. Similar to the recently reported biphenylene-containing diazaacene **3** (Figure 1 b),^[7] molecules **1a** and **1b** can be regarded as a result from combining N-heteroacene and

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or a C–C single bond to extend N-heteroacenes for a new design of n-type semiconductors in terms of the spatial delocalization and energy level of LUMO as well as the reorganization energy. In solution-processed thin film transistors, the π -extended N-heteroacenes are found to function as ntype semiconductors with field effect mobility of up to 0.02 cm²V⁻¹s⁻¹ under ambient conditions.



Figure 1. a) Structures of π -extended N-heteroacenes (**1 a**,**b**) and the corresponding N-heteroacenes (**2 a**,**b**); b) structures of related molecules.

[*N*]phenylene, the latter of which formally has benzene rings fused to cyclobutadiene moieties in an alternating manner.^[8] But unlike **3**, molecules **1a**,**b** contain a moiety of cyclobuta[1,2-*b*:3,4-*b'*]diquinoxaline (**4** in Figure 1b)^[9] rather than biphenylene. To better understand the effect of the four-membered ring in π -extension of N-heteroacenes, **2a**,**b**, two unprecedented tetraazaacenes were also synthesized as reference compounds in this study. Detailed below is an exploratory study on **1a**,**b** with experimental and computational methods in comparison to tetraazaacenes **2a**,**b** with a focus on synthesis, structures, and solution-processed OTFTs.



Results and Discussion

As shown in Scheme 1, compound **1 a** was synthesized by Pdcatalyzed coupling of phenylenediamine **6 a**^[10] with 2,3-dibromo-cyclobuta[1,2-*b*:3,4-*b'*]diquinoxaline (**5**), which was prepared by modifying the recently reported synthesis of chlorinated cyclobuta[1,2-*b*:3,4-*b'*]diquinoxaline.^[11] Using 1,1'-bis(diphenylphosphino)ferrocene (dppf) as the ligand and Cs₂CO₃ as



Scheme 1. Synthesis of 1 a,b. Reagents and conditions: a) $Pd(PPh_3)_4$, dppf, Cs₂CO₃, toluene, 120 °C; b) MnO₂, CH₂Cl₂.

the base,^[12] this Pd-catalyzed coupling reaction yielded **1a** as a mixture with its dihydro derivative **7a**, which could be separated into **1a** and **7a** in pure form. Oxidation of the mixture of **1a** and **7a** with MnO₂ resulted in pure **1a** in a yield of 26% from **5**. In a similar manner, compound **1b** was synthesized by Pd-catalyzed coupling of **5** with naphthalenediamine **6b**,^[13] which was prepared from 4,9-dibromonaphtho[2,3-c][1,2,5]thiadiazole,^[14] as detailed in the Supporting Information. However, the Pd-catalyzed coupling reaction only yielded the dihydro derivative **7b**, which was then oxidized by MnO₂ to **1b** in a high yield. As detailed in the Supporting Information, **2a** and **2b** were synthesized by Pd-catalyzed coupling of the corresponding diamines (**6a** and **6b**, respectively) with 6,7-dibromoquinoxaline and subsequent oxidation with MnO₂.

It was found that compounds **1a** and **1b** are stable toward air and heating. After exposure to ambient light and air at room temperature for 10 days, solutions of **1a** and **1b** in CDCl₃ did not exhibit any apparent change, as monitored with ¹H NMR (Figures S1 and S2 in the Supporting Information). Heating the solids of **1a** and **1b** at 200 °C in air for 2 h did not result in any chemical changes, as found from the ¹H NMR spectra of the solutions of the heated solids (Figures S5 and S6 in the Supporting Information). In contrast, the reference compounds **2a** and **2b** appeared to be unstable when their solids were heated at 200 °C in air for 2 h, as monitored with ¹H NMR in the same way, although they exhibited similar stability as **1a** and **1b** in solution under ambient conditions. To better understand π -extension through the four-membered ring, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **1***a*,**b** and **2***a*,**b** were studied in a comparative manner with both experimental and computational methods. Figure 2a compares the



Figure 2. UV/Vis spectra for 0.01 mm solutions of 1 a and 2 a (a) and 1 b and 2 b (b) in hexane.

UV/Vis absorption spectra of 1a and 2a, showing that 1a has redshifted and more intense absorption relative to 2a in the visible light region. Similarly, Figure 2b compares the UV/Vis absorption spectra of 1b and 2b showing that the longestwavelength absorption of 1b shifts to red by 52 nm relative to that of 2b. Such redshifted absorption of 1a and 1b relative to the corresponding N-heteroacenes (2a and 2b, respectively) is similar to the reported absorption spectra of phenylene-containing oligoacenes, which are redshifted relative to the corresponding oligoacenes.^[15] In the test window of cyclic voltammetry, 1 a,b and 2 a,b all exhibited two quasi-reversible reduction waves (Figure S14 in the Supporting Information). Based on the first reduction potentials^[16] as well as the absorption edges found from the UV/Vis absorption spectra, the LUMO and HOMO energy levels of 1 a,b and 2 a,b are estimated and summarized in Table 1. It is found that, from 2a to 1a, the LUMO is lowered by 0.30 eV, whereas the HOMO is lowered by only 0.13 eV. Similarly, from 2b to 1b, the LUMO is lowered by 0.20 eV, whereas the HOMO is lowered by only 0.08 eV.

The frontier molecular orbitals of **1** a,b and **2** a,b were calculated using simplified model molecules (**1** a',b' and **2** a',b' in Figure S15 in the Supporting Information), which have smaller trimethylsilyl groups replacing the triisopropylsilyl groups.^[17] The geometries of these model molecules were 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. As shown in Figure 3a, an interesting finding from the calculated orbitals is that the LUMOs of **1** a,b are fully delocalized in the polycyclic

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Table 1. Absorption, reduction potentials, and frontier molecular orbita
energy levels of 1 a,b and 2 a,b.

	λ _{max} [nm] ^[a]	Gap [eV] ^[b]	Experim E _{red} ¹ [V] ^[c]	ental LUMO [eV] ^[d]	HOMO [eV] ^[e]	C LUMO [eV]	alculated HOMO [eV]	^{ff]} Gap [eV]
1a	570	2.11	-0.77	-4.33	-6.44	-3.89	-6.09	2.20
1b	737	1.63	-0.68	-4.42	-6.05	-3.97	-5.64	1.67
2a	525	2.28	-1.07	-4.03	-6.31	-3.61	-6.06	2.45
2b	685	1.75	-0.88	-4.22	-5.97	-3.79	-5.62	1.83

[a] The maximum of the longest-wavelength absorption band (λ_{max}) from a 0.01 mM solution in hexane. [b] HOMO–LUMO gap as estimated from the absorption edge from the same solution. [c] Half-wave potential versus ferrocenium/ferrocene. [d] Estimated from LUMO = $-5.10-E_{red}^{-1}$ (eV). [e] Calculated from the HOMO–LUMO gap and the LUMO energy level. [f] Calculated at the B3LYP level of DFT with 6-311 + +G(d,p)//6-31G(d,p) basis sets using simplified model molecules (1 a',b' and 2 a',b').



Figure 3. a) Calculated frontier molecular orbitals of **1** a' and **1** b'; b) structures of **8** a-c; c) calculated frontier molecular orbitals of **8** a-c.

backbone while the HOMOs of **1a,b** are localized on the tetraazaacene moieties. In agreement with this, the LUMO energy levels of **1a** and **1b** are lower than **2a** and **2b**, respectively, whereas the HOMO energy levels of **1a** and **1b** are essentially the same as those of **2a** and **2b**, respectively. Moreover, the calculated HOMO and LUMO energy levels of **1a,b** are consistent with the finding from the experimental values that from **2a** to **1a** and from **2b** to **1b**, the LUMO energy level is lowered by a larger degree than the HOMO energy level, leading to the observed redshift of longest-wavelength absorption of **1a,b** relative to **2a,b**.

Similar to 1 a,b, biphenylene-containing diazaacenes (e.g., 3) were also reported to have the LUMO delocalized in the whole polycyclic backbone but the HOMO localized on the diazaacene moiety.^[7] To better understand the unequal distribution of HOMO and LUMO of 1 a,b, we calculated molecules 8 a, 8 b, and 8c (Figure 3b), which have tetraazapentacene and guinoxaline linked together by a four-membered ring, a five-membered ring, and a C-C single bond, respectively. As found from the energy-minimized models (Figure S16 of the Supporting Information), 8a is a planar molecule having two C-C single bonds of 1.495 Å long in the four-membered ring. The tetraazapentacene and quinoxaline subunits in 8b and 8c are in the same plane but are linked by shorter C-C bonds, as shown with bold lines in Figure 3b. These calculated bond lengths suggest that 8a has poorer conjugation between the tetraazapentacene and guinoxaline subunits than 8b and 8c. It was found that 8a-c all have their HOMOs localized on the tetraazapentacene moiety, as shown in Figure 3 c, indicating that the localized HOMO is due to the unsymmetrical molecular structures rather than the linker. As shown in the same figure, the LUMO of 8a is delocalized over the whole molecule and evenly distributed on the tetraazapentacene and quinoxaline moieties, whereas those of 8b and 8c are more localized on the tetraazapentacene moiety. In agreement with the even distribution, the LUMO of 8a has a lower energy level than those of **8b**,**c**, as summarized in Figure 3c.

With greater spatial delocalization and lower energy level of LUMO, 8a is a better candidate for n-type semiconductors than 8b and 8c. With this idea in mind, we further calculated the inner reorganization energy for electron transport (λ_{e}), which is a key parameter determining electron transfer rate in n-type organic semiconductors.^[18] As the reorganization energy for electron transport is due to geometric relaxation accompanying a self-exchange electron-transfer reaction between a neutral molecule and a neighboring radical anion, a smaller reorganization energy leads to a larger electron mobility.^[19,20] It is found that the reorganization energy of 8a (0.132 eV) is lower than those of 8b (0.148 eV), and 8c (0.173 eV). Moreover, the reorganization energy of 1 b' for electron transport (0.153 eV) is lower than that of 2b' by 0.041 eV. These reorganization energies for electron transport suggest that the four-member ring is a promising linker to extend Nheteroacenes for a new design of n-type organic semiconductors.

Single crystals of **1b** selected for X-ray crystallography were grown by slow diffusion of acetone vapor into a solution of

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Figure 4. Crystal structure of **1b**: a) the polycyclic backbone of **1b** with some atoms labeled and some bond lengths highlighted; b) π - π interactions between molecules of **1b**. (C and N atoms in the polycyclic backbone are shown as ellipsoids at 50% probability and the substituents are shown as sticks. H atoms are removed for clarification.)

1b in toluene.^[21] The crystal structure of **1b** exhibits an essentially flat backbone as shown in Figure 4a. Examination of the bond lengths of 1b reveals that its central four-membered ring contains four single C-C bonds. Two of them (C14a-C14b and C8a-C8b) are 1.50 Å long, which is even longer than that of the typical nonconjugated single bond between two sp²-hybridized C atoms (1.47-1.48 Å).^[22] Such long C-C bonds are in agreement with the calculated bond length of 8a, indicating that these two bonds do not involve any π characters. This is in agreement with the earlier conclusion that the π bonds in [N]phenylenes are localized within the six-membered rings.^[15,23] The bond of C14b–C8a, having a bond length of 1.46 Å, is longer than typical C=C double bonds in alkenes (1.31–1.34 Å) and typical C–C 1.5 bonds in arenes (1.38– 1.40 Å), but represents a conjugated single bond between two sp²-hybridized C atoms with a typical bond length of 1.45-1.46 Å.^[22] Although slightly shorter than C14b–C8a, the bond of C8b-C14a still has a bond length (1.43 Å) close to that of a typical conjugated single bond between two sp²-hybridized C atoms. The four-membered ring is attached to four N atoms with four short C–N bonds (1.28 Å for C8a–N8 and C14b–N15; 1.30 Å for C8b–N9 and C14a–N14), which are shorter than typical C=N double bonds in imines (1.35 Å),^[22] as well as other C-N bonds in the same molecule. These bond lengths, similar to the corresponding bond lengths in molecule 4,^[11] present a radialene-like structure, presumably because 1b needs to avoid an antiaromatic cyclobutadiene structure.

The crystal structure of $1\,b$ exhibits infinite $\pi\text{-stacks}$ in two directions that intersect with an angle of 68.0° (Figure S18 in the Supporting Information). As shown in Figure 4b, in each

direction molecules of **1b** are arranged in a one-dimensional face-to-face π -stack with head-to-tail overlap, which is similar to the reported molecular packing of 1,4-silylethynyl-substituted dihydrohexaazapentacene.^[24] It is found that neighboring molecules of **1b** stack with each other with two slightly different arrangements alternating in one stack. One arrangement has the two π -faces separated by 3.31 Å and the two silicon atoms of neighboring molecules separated by 11.47 Å. In comparison, the other arrangement has two π -faces separated by 3.34 Å and the two silicon atoms of neighboring molecules separated by 7.34 Å, which is accompanied with a shift along the long axis of the polycyclic backbone. The distances between the π -planes of **1b** in the crystal are slightly smaller than double the van der Waals radius (1.70 Å) of carbon.

To test semiconductor properties of **1 a,b** in OTFTs, their thin films were dip-coated onto a silicon substrate, which had successive layers of silica, alumina, and 12-cyclohexyldodecylphosphonic acid (CDPA, as shown in Figure 5 a) as a composite dielectric material. Here, CDPA formed a self-assembled monolayer (SAM) on alumina to passivate surface hydroxyl groups and



Figure 5. a) Phosphonic acid that is used to modify the Al_2O_3/SiO_2 dielectric surface in the OTFTs; b) drain current (I_{DS}) versus gate voltage (V_G) with drain voltage (V_{DS}) at 30 V for OTFT of **1 b** with an active channel of W = 1 mm and $L = 150 \mu$ m as measured in air.

to provide a highly ordered dielectric surface wettable by common organic solvents^[25] and the resulting CDPA-Al₂O₃/SiO₂ had a capacitance per unit area (Ci) of $26 \pm 1 \text{ nF cm}^{-2}$.^[26] Thin films of 1a and 1b were formed by immersing the CDPA- Al_2O_3/SiO_2 substrate into a solution (CH₂Cl₂/acetone, 3:1 by volume for 1a and CH_2Cl_2 for 1b) and then pulling it up with a constant speed of 1.7 μ m s⁻¹. The dip-coated films of **1a** and 1b consisted of aligned crystal fibers as shown in the polarized-light micrograph in Figure S23 (see the Supporting Information). The X-ray diffraction (XRD) from the film of 1a exhibited a diffraction at $2\theta = 5.19^{\circ}$ (d spacing = 17.0 Å) accompanied with two higher-order peaks with d spacing of 8.5 Å and 5.7 Å, suggesting a lamellar structure. The dip-coated film of 1b exhibited one peak at $2\theta = 5.35^{\circ}$ (d spacing = 16.5 Å), which does not correspond to any diffraction derived from the single crystal structure, indicating a polymorph different from the singlecrystal phase. The fabrication of OTFTs was completed by vacuum-deposition of gold on the dip-coated organic films through a shadow mask to form top-contact source and drain



electrodes. As measured from 30 channels in air, **1b** functioned as an n-type semiconductor with field effect mobility of $0.015 \pm 0.004 \text{ cm}^2 \text{V}^{-1}\text{s}^{-1}$. Shown in Figure 5 b are the transfer *I*– *V* curves measured from a typical OTFT of **1b** in its saturation regime. By contrast, the films of **1a** exhibited field-effect mobility of $(1.5 \pm 0.7) \times 10^{-3} \text{ cm}^2 \text{V}^{-1}\text{s}^{-1}$, which was one order of magnitude lower than that of **1b**. For comparison, thin films of **2a** and **2b** were fabricated with the same method. It was found that the film of **2b** functioned as an n-type semiconductor with field-effect mobility of $(4.1 \pm 2.0) \times 10^{-3} \text{ cm}^2 \text{V}^{-1}\text{s}^{-1}$ as measured in air, whereas the film of **2a** behaved as an insulator, which can be attributed to the discontinuous crystal grains in the film (Figure S23 in the Supporting Information).

N-channel OTFTs usually exhibit higher field effect mobility under vacuum than in air because oxygen and water in air can diffuse into the organic films and guench mobile electrons. To our surprise, when the OTFTs of 1b were placed in the vacuum chamber of a probe station for a few hours to remove oxygen and water residues and then tested under the same vacuum, the measured field effect mobility of 1b decreased to the range of 10^{-3} cm²V⁻¹s⁻¹. Further study with XRD revealed that the vacuum promoted a phase transition of **1 b** in the dipcoated films, as shown in Figure S25 (see the Supporting Information), and the resulting new polymorph showing a diffraction at $2\theta = 5.89^{\circ}$ (d spacing = 15.0 Å) was also different from the single crystal phase. As observed with a polarized light microscope, such phase transition was accompanied with formation of cracks on the crystal fibers of 1 b. Therefore, the lower mobility of 1b, as measured under vacuum, may be attributed to the second thin-film phase and formation of cracks. In contrast, the OTFTs of **2b** increased to 0.15 ± 0.04 cm²V⁻¹s⁻¹ when measured under vacuum. This also suggests that the mobility of 1b measured in this study is likely an underestimation of the intrinsic value, and higher mobility might be achieved with optimized conditions for fabrication and measurement.

Conclusions

In summary, this study puts forth a new family of π -extended N-heteroacenes by connecting a large tetraazaacene and quinoxaline through a four-membered ring. On the basis of the crystal structure and DFT calculation, it is concluded that the $\boldsymbol{\pi}$ bonds in 1a and 1b are localized within the six-membered rings, in agreement with the earlier conclusion on [N]phenylenes. Interestingly, 1a and 1b exhibit unequal distribution of HOMO and LUMO, having their LUMOs delocalized in the whole polycyclic backbone but their HOMOs localized on the tetraazaacene subunit, owing to their unsymmetrical molecular structures. As found from the DFT calculation, the four-membered ring is a better linker than a five-membered ring or a C-C single bond to extend N-heteroacenes for a new design of n-type semiconductors in terms of the spatial delocalization and energy level of LUMO and the reorganization energy. In agreement with this, 1a and 1b are found to function as ntype organic semiconductors in solution-processed thin-film transistors.

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