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Hydrogen-Bonded Dihydrotetraazapentacenes

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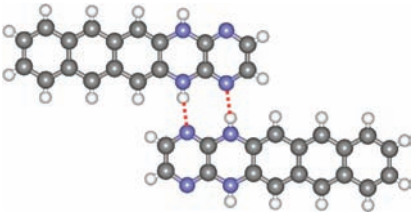
ABSTRACT



Three new members of *N*-heteropentacenes explored herein have adjacent pyrazine and dihydropyrazine rings at one end of the pentacene backbone. Interesting findings from this study include self-complementary N−H···N H-bonds in the solid state, solvent-dependent UV−vis absorption caused by H-bonding, and new *p*-type organic semiconductors with field effect mobility up to 0.7 $cm^2 V^{-1} s^{-1}$.

N-heteropentacenes, which have N atoms inserted into the backbone of pentacene, have recently been found as a new family of organic semiconductors with high performance in organic thin film transistors (OTFTs).[1] A combination of varied number, position, and valence state of N atoms in *N*-heteropentacenes can in principle yield a large number of structurally related π-backbones and thus provide good opportunities for developing novel organic semiconductors and studying structure−property relationship. Unlike pentacene, *N*-heteropentacenes are capable of H-bonds with N atoms. As found from the known crystal structures, *N*-heteropentacenes can form not only classical H-bonds (N−H···O and N···H−O) with solvent molecules,[2,3] but also weak H-bonds (C−H···N) with each other.[4] Because of the greater strength, classical H-bonds are in principle more powerful in directing the molecular packing of *N*-heteropentacenes. However, classical H-bonds between *N*-heteropentacene molecules have not been reported to the best of our knowledge.

To explore how classical H-bonds (N−H···N) tune the properties of *N*-heteropentacenes, we designed a new dihydrotetraazapentacene (**1**) that has adjacent pyrazine and dihydropyrazine rings at one end of the pentacene backbone as shown in Figure 1. This design allows self-complementary N−H···N H-bonds in the solid state as detailed in this letter. Following the success of silylethynylated pentacene[5] and *N*-heteropentacenes[4,6] as soluble and stable organic semiconductors with high charge carrier mobility, triisopropylsilylethynyl groups are introduced to **1** leading to **2** and **3**. Particularly, the NH groups of **2** are exposed as found from the space-filling model shown in Figure 1b and thus are available for H-bonding. On the other hand, the NH groups of **3** are shielded by the bulky triisopropylsilyl groups and thus are unavailable or at least much less available for H-bonds with a H-bond acceptor. Studying UV−vis absorption of **2** and **3** in different solvents has led to an interesting finding on solvent-dependent absorption caused by H-bonding. It is found that both **1** and **3** function as *p*-type organic semiconductors in thin film transistors, and **3** exhibits field effect mobility as high as 0.7 $cm^2 V^{-1} s^{-1}$.

Shown in Scheme 1 are the syntheses of **1**−**3** in two ways. **1** and **2** were synthesized from 2,3-diaminopyrazine

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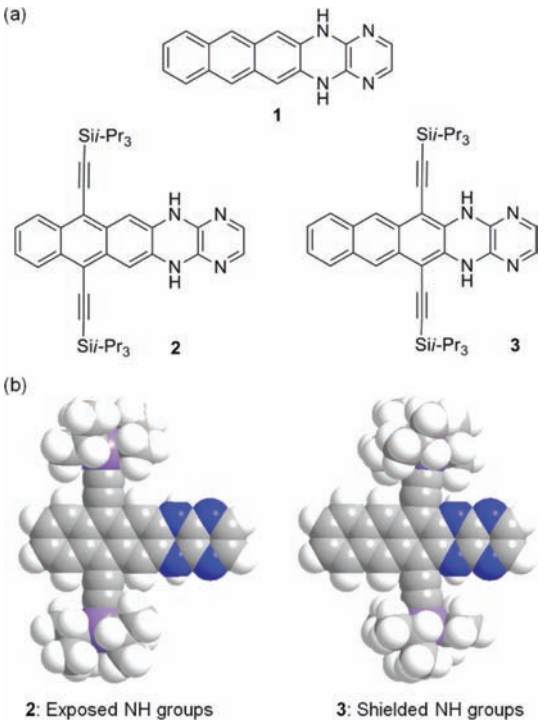

Figure 1. (a) Molecular structures of 5,14-dihydro-1,4,5,14-tetraazapentacene (**1**) and its ethynylated derivatives (**2** and **3**). (b) Space-filling models of **2** and **3** as optimized at B3LYP/6-31g(d,p) level of density functional theory (DFT) (C, N, Si, and H atoms are shown in gray, blue, violet, and white, respectively).

and the corresponding dihydroxyanthranenes (**4**[2] and **5**, respectively) by solvent-free condensation at 205−215 °C. The new compound **5** was prepared from 2,3-dimethoxyanthracene[2] in five steps as detailed in the Supporting Information. The low yield of **2** may be attributed to the low stability of **5** at high temperature. Unlike its constitutional isomer **2**, **3** was synthesized by Pd-catalyzed coupling of **6**[7] and 2,3-dichloropyrazine using 1,1′-bis(diphenylphosphino)ferrocene (dppf) as ligand and Cs_2CO_3 as base. This condition was a modification from Bunz's recent synthesis[8] of an isomer of **2** and **3** from 2,3-dichloroquinoxaline and 1,4-bis(triisopropylsilylethynyl)-2,3-diaminonaphthalene using biaryl phophane ligand and Hünig's base.

Molecules **1**−**3** may each in principle exist as three isomers by varying the position of H atoms that are bonded to N atoms. As the representative, the three isomers of **1** are shown in Figure 2. According to Clar's aromatic sextet rule,[9] **1** is more energetically favorable than **1**′ and **1**″ because **1** has two aromatic sextet rings, while **1**′ and **1**″ have only one. The ^{1}H NMR of **1** shows four singlet peaks and two sets of peaks

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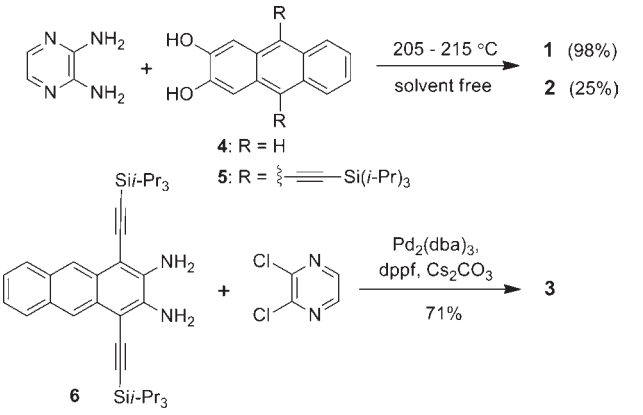
Scheme 1. Synthesis of **1**−**3**



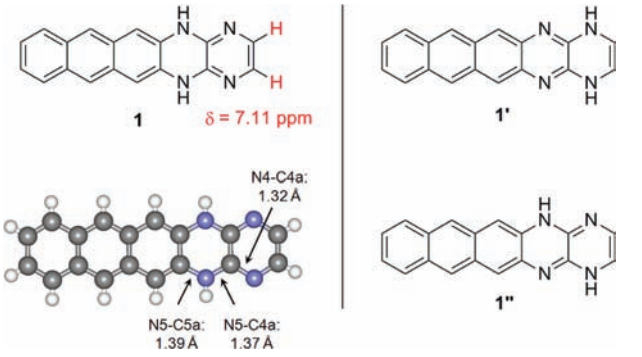


Figure 2. Possible isomeric structures of **1** and the crystal structure of **1** (C, N, and H atoms are shown in gray, blue, and white, respectively).

with characteristic AA′XX′ patterns, in agreement with the C_{2v} symmetry, thus excluding the structure of **1**″. Moreover, the H2 and H3 of **1** (shown in red in Figure 2) exhibit a chemical shift at 7.11 ppm, which is very close to the chemical shift (7.13 ppm) of the corresponding H atoms in 2,3-diaminopyrazine.[10] As shown in Figure 2, the N5−C5a and N5−C4a bonds are both longer than the N4−C4a bond, and the N5−C5a bond has the same length as the N−C bond (1.39 Å) in 6,13-dihydro-6,13-diazapentacene.[2] These bond lengths support the structure of **1**, which has dihydropyrazine as the second ring.

Compound **1** is only soluble in DMSO and DMF, while **2** and **3** are soluble in a variety of organic solvents including benzene, CH_2Cl_2, acetone, and THF. Dissolving **2** and **3** in varied solvents has led to an interesting finding that **2** exhibits an apparent solvent-caused color change, while **3** almost keeps the same color in different solvents. As shown in Figure 3a, a solution of **2** in CH_2Cl_2 appears yellow, but that in DMSO appears orange. This color change is accompanied with a red shift of longest-wavelength

(10) The ^{1}H NMR spectra of **1** and 2,3-diaminopyrazine were both measured in DMSO-d_6.

absorption by 35 nm. Such solvent-dependent color change may possibly be related to solvatochromism, which is a well-known phenomenon of color change due to a change in solvent polarity. The widely accepted explanation for solvatochromism is that the ground state and the Franck−Condon excited state of a polar chromophore are stabilized by polar solvent molecules with different degree.[11] To determine whether the solvent-caused color change of **2** is a solvatochromic effect, the absorption spectra of **2** were recorded in varied solvents. As shown in Figure 3b, the measured values of longest-wavelength absorption were first plotted against the dielectric constant of the corresponding solvent. The data for **2** show neither positive nor negative correlation between the longest-wavelength absorption and the solvent dielectric constant, indicating that the solvent-caused color change of **2** can not be described with classical solvatochromism.

On the other hand, the chemical shift for N−H of **2** exhibits a downfield shift from 6.81 ppm to 10.49 ppm when the solvent changes from CD_2Cl_2 to DMSO-d_6, indicating formation of H-bonds between **2** and DMSO. To test the effect of H-bonding on absorption, the measured values of longest-wavelength absorption were plotted against the solvent H-bond basicity parameter (pK_{HB})[12] as shown in Figure 3c. The positive correlation presented in Figure 3c indicates that the solvent-caused color change of **2** in fact depends on the H-bond basicity of solvents. This dependence can be understood in terms of the H-bonded complex **2**·2Sol and its resonance form **2′**·2Sol as shown in Figure 3d. The resonance form **2′** is expected to contribute to the longer-wavelength absorption because it has a diazatetracene substructure with greater conjugation. Therefore, the factors that stabilize **2′** can lead to a red shift of absorption band. The higher H-bond basicity a solvent has, the stronger H-bond it forms with **2**. A stronger H-bond weakens the N−H bond by a greater degree, leading to a more negative charge on the N atoms. Such H-bond-induced negative charge can partially counterbalance the positive charge on N atoms in **2′** and thus stabilize this resonance form. As stabilized by stronger H-bonds, **2′** can make greater contribution to the resonance structure of **2**, leading to red-shifted absorption. In contrast, the longest-wavelength absorption of **3** only exhibits a very small red shift when the solvent is changed from CH_2Cl_2 to DMSO as shown in Figure 3c because its shielded N−H groups are much less available, if not unavailable, for H-bonds with solvent molecules.

Single crystals of **1** and **3** were grown by physical vapor transport and from solution in ethyl acetate, respectively. X-ray crystallographic analysis on the single crystals of **1** and **3** has revealed their molecular packing. Molecules of **1** form H-bonded ribbons, which stack in two directions. As shown in Figure 4a, molecules of **1** are linked by double N−H···N H-bonds, which have the N-to-N distance

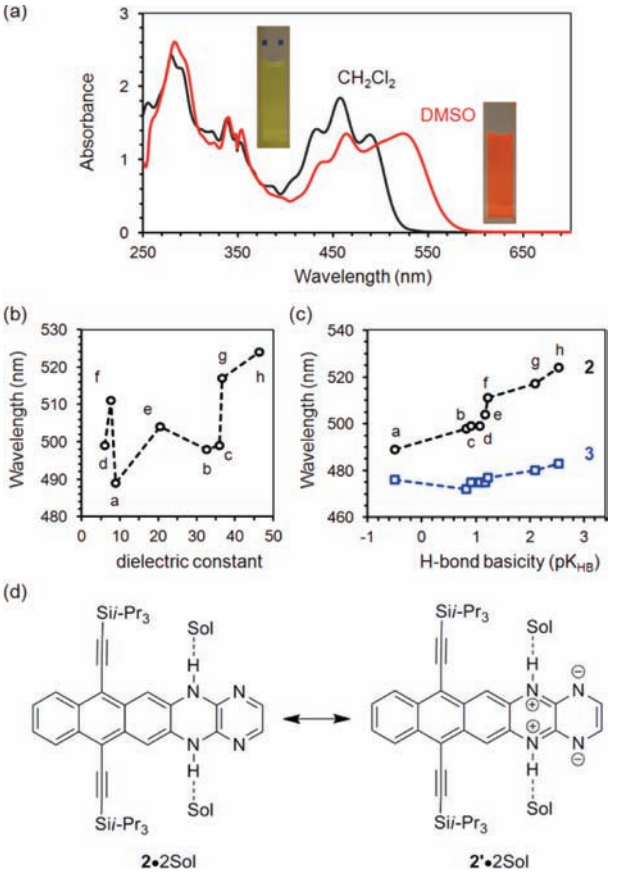


Figure 3. (a) Absorption spectra of **2** in CH_2Cl_2 and DMSO (5×10^{-5} mol/L). (b) The longest-wavelength absorption of **2** in varied solvents versus the dielectric constant of solvent (a: CH_2Cl_2, b: CH_3OH, c: CH_3CN, d: ethyl acetate, e: acetone, f: THF, g: DMF, h: DMSO). (c) The longest-wavelength absorption of **2** and **3** in varied solvents versus the H-bond basicity of solvent. (d) Resonance structures for H-bonded complex of **2** and solvent molecules (Sol).

of 3.05 Å, the H-to-N distance of 2.25 Å, and the N−H−N angle of 154.7°. Two π-stacked molecules of **1** are separated by a distance of 3.42 Å between π-planes and have an offset arrangement with a relative shift along the long molecular axis. In the crystal lattice, each molecule of **1** occupies a volume of 320.14 Å^3, which is smaller than the volume occupied by 6,13-dihydro-6,13-diazapentacene (332.15 Å^3 per molecule)[2] and 6,13-diazapentacene (333.89 Å^3 per molecule).[13] This suggests that H-bonds between *N*-heteropentacene molecules can be helpful in forming denser packing. As shown in Figure 4b, **3** exhibits π-stacking of two-dimensional brickwork arrangement, which is typical of silylethynylated pentacenes[5] and *N*-heteropentacenes.[4,6] The distance between π planes of **3** is 3.35−3.37 Å. No H-bonds are found between molecules of **3** in the crystal structures in agreement with the shielded NH groups.

Semiconductor properties of **1** and **3** were tested in vacuum-deposited thin film transistors, which have octadecyltrimethoxysilane (OTMS) modified 300 nm-thick

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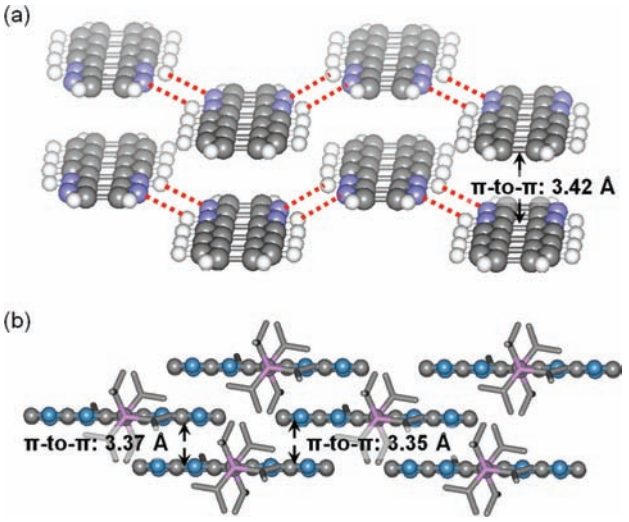

Figure 4. Molecular packing of **1** and **3** in crystals: (a) H-bonds (shown as red dashed lines) and π-stacks of **1**; (b) brickwork π-stacks of **3**. The *N*-heteropentacene cores are shown as ball-stick model and the silylethynyl substituents are shown in stick model. H atoms are removed for clarification. The grayish-blue colored atoms of **3** contain both N and C atoms due to disorder.

SiO_2 as dielectrics,[14] vacuum-deposited gold as top-contact drain and source electrodes, and heavily doped silicon as a bottom gate electrode. However, efforts to fabricate devices from **2** by thermal evaporation failed because it decomposed during heating under vacuum. The X-ray diffractions (XRD) from the films of **1** did not show any peaks indicating the amorphous nature of **1** in the film. On the other hand, XRD from **3** (shown in the Supporting Information) exhibited four peaks in accordance with the (001), (002), (003), and (005) diffractions derived from the single crystal structure, indicating a highly crystalline film. It is found that both **1** and **3** function as *p*-type semiconductors with field effect mobility of $4-7 \times 10^{-4}$ and 0.3–0.7 $cm^2\ V^{-1}\ s^{-1}$, respectively. The *p*-type semiconductor behaviors of **1** and **3** are in agreement with their energy levels of highest occupied molecular orbital (HOMO) at −4.80 eV and −5.17 eV, respectively, which were estimated from the irreversible oxidation waves in the cyclic voltammograms (see the Supporting Information). The low field effect mobility of **1** should be attributed to the amorphous nature of its vacuum-deposited film, as it is well-known that the field effect mobility is very sensitive to the crystallinity of the thin film.[15] The disordered arrangement of **1** in the thin films prevents evaluating the effect of H-bonding on charge transport by comparing the field effect mobility of **1** with those of other *N*-heteropentacenes that do not form H-bonds in the solid state. Shown in Figure 5 are the transfer $I-V$ curves for the best-performing OTFT of **3**, which exhibits a field-effect mobility of 0.7 $cm^2\ V^{-1}\ s^{-1}$ and an on/off ratio of 3×10^5 for drain current between 0 and −80 V gate bias.

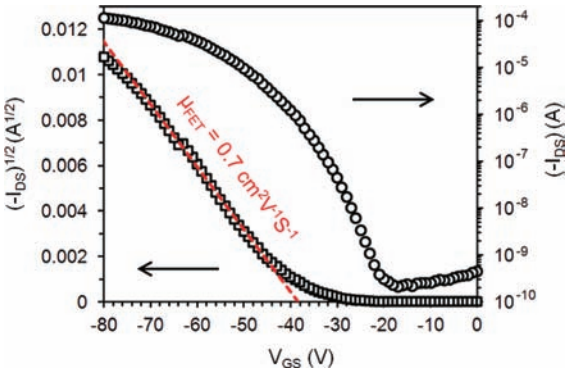

Figure 5. Drain current (I_{DS}) versus gate voltage (V_{GS}) at drain voltage (V_{DS}) of −80 V for an OTFT of **3** with the active channel of $W = 1$ mm and $L = 50\ \mu$m as measured in air.

In conclusion, the above study has explored three new members of *N*-heteropentacenes that have adjacent pyrazine and dihydropyrazine rings at one end of the pentacene backbone. This design not only allows self-complementary N−H···N H-bonds in the solid state, but also leads to interesting findings on solvent-dependent UV−vis absorption, which can be attributed to H-bonds with solvent molecules. Two of the compounds are found to function as *p*-type semiconductuors in OTFTs. Further investigation on single-crystal transistors of **1** may allow evaluating the effect of H-bonding on charge transport.

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Supporting Information Available. Details of synthesis, cyclic voltammetry, UV−vis absorption, DFT calculation, fabrication and characterization of thin film transistors, NMR spectra, and CIF files for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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