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# N-Phenylated N-Heteroacenes: Synthesis, Structures and Properties

#### Xiao Gu, Bowen Shan, Zikai He§ and Qian Miao\*

**Abstract:** Herein we report two novel N-phenylated Nheteroacenes (1 and 2) detailing their synthesis, structures and properties. 1 is a N-hetero analogue of rubrene, but differs from rubrene by having a bent backbone and behaving as an insulator in the solid state due to lack of  $\pi$ - $\pi$  interactions. 2 is a N-hetero analogue of 6,13-diphenylpentacene (DPP) with essentially the same molecular geometry and crystal packing as DPP, but exhibiting field effect mobility higher than that of DPP by two orders of magnitude.

Functionalization of acenes<sup>[1]</sup> and N-heteroacenes<sup>[2, 3, 4]</sup> with various substituting groups has led to a family of organic semiconductors. The most successful functional groups for this strategy are (trialkylsilyl)ethynyl groups, which were first introduced by Anthony to acenes [5] and later applied to Nheteroacenes <sup>[6, 7]</sup> resulting in a few solution-processed organic semiconductors with high field effect mobility in orgnaic thin film transistors (OTFTs).<sup>[8]</sup> Unlike acenes, N-heteroacenes can be functionalized by attaching substituents to not only C atoms but also N atoms. However, N-functionalization has been less explored than C-functionalization for N-heteroacenes. The known N-functionalized N-heteroacenes were synthesized by direct N-alkylation of N-heteropentacenes <sup>[9, 10]</sup> or by attaching phenyl groups to N atoms in the synthetic precursors of Nphenylated N-heteroacenes.<sup>[11]</sup> Here, we report synthesis of two new members of N-phenylated N-heteroacenes, 1 and 2, by Nphenylation of N-heteroacenes. As shown in Figure 1, 1 is a Nhetero analogue of rubrene, a leading p-type organic semiconductor with high field effect mobility of up to 40 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> as measured from single crystal transistors,<sup>[12, 13, 14]</sup> and **2** is a N-hetero analogue of 6,13-diphenylpentacene (DPP), a p-type organic semiconductor with low field mobility  $(10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$  in thin films.  $^{\left[ 15\right] }$  In the following study, we compare 1 and 2 with their hydrocarbon analogues in terms of structures and properties to better understand the structure-property relationship.

Scheme 1 shows the synthesis of 1 starting from 6,11dibromo-5,12-diazatetracene (3).<sup>[16]</sup> The Suzuki coupling of 3

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with phenylboronic acid resulted in 6,11-diphenyl-5,12diazatetracene (4). Nucleophilic addition of phenyl lithium to 4 yielded 5, which was used in the next step without purification. The Buchwald–Hartwig coupling reaction  $^{[17]}$  of 5 with iodobenzene using (*t*-Bu)<sub>3</sub>P as ligand yielded 1 as a yellow solid. Similarly, the Buchwald–Hartwig coupling reaction of 6,13dihydro-6,13-diazapentacene (6)  $^{[18]}$  with iodobenzene using 2dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (RuPhos) as the ligand yielded 2 in a moderate yield.



Figure 1 Structures of N-phenylated N-heteroacenes 1 and 2 as well as their hydrocarbon analogues.



Scheme 1 Synthesis of 1 and 2.

Single crystals of **1** qualified for X-ray crystallography were grown slow evaporation of *n*-hexane solution, while those of **2** were grown by sublimation in a physical vapor transport (PVT) system.<sup>[19]</sup> Figure 2 compares the crystal structures of **1** <sup>[20]</sup> and rubrene.<sup>[21]</sup> As shown in Figure 2a and b, the crystal structure of **1** exhibits a significantly bent backbone with an angle of 142.7°

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between the naphthalene plane and the benzene plane (Figure 2b), in agreement with sp<sup>3</sup> hybridized N atoms. The four C-N bonds (shown in red in Figure 2a) in the dihydropyrazine ring have bond lengths of 1.42 to 1.44 Å and are longer than the corresponding C-N bonds in 2 (shown in red in Figure 3b) by 0.2 to 0.4 Å, suggesting poorer conjugation between the benzene ring and the N atom in the tetracene backbone of 1. In contrast, rubrene in the crystal has an essentially flat tetracene backbone, which is surrounded with four substituting phenyl groups roughly parallel to each other and roughly perpendicular to the tetracene plane as shown in Figure 2c. Unlike the phenyl substituents in rubrene, the two substituting phenyl rings on N atoms in 1 are roughly perpendicular to each other. The different molecular geometries of 1 and rubrene suggest that 1 has a more flexible backbone than rubrene, in agreement with poor conjugation between the benzene rings in the backbone. The observed molecular geometry of 1 is a result of bending the backbone to avoid repulsions between the neighboring phenyl substituents. With the bent backbone and unsymmetrical arrangement of phenyl substituents, 1 is chiral and its crystal lattice consists of a pair of enantiomers, which pack in an alternate arrangement without  $\pi - \pi$  interactions between the tetracene backbone. Instead, as shown in Figure 2b, edge-to-face interactions are found between a phenyl substituent and the naphthalene moiety with a H-to-C contact (2.86 Å) shorter than the sum of van der Waals radii of H and C atoms as shown in Figure 2b. In contrast, rubrene exhibits a slipped  $\pi$ - $\pi$  stacking between neighboring tetracene backbones with a  $\pi$ -to- $\pi$  distance of 3.72 Å as shown in Figure 2d.



Figure 2 (a) Structure and (b) molecular packing of 1 in the single crystal; (c) structure and (d) molecular packing of rubrene in the single crystal. <sup>[22]</sup> (C, N atoms are shown as grey and blue ellipsoids, respectively, at 50% probability level.)

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Figure 3a and b show the crystal structure of 2,<sup>[20]</sup> which has an essentially flat pentacene backbone with slight bending along its long axis, suggesting the two N atoms are  $sp^2$  hybridized. Unlike 1, molecule 2 does not need to bend its backbone because its phenyl substituents do not experience repulsions from crowdedness. The four C-N bonds (shown in red in Figure 3b) in the central ring are 1.40 Å long. The shorter bond length of these C-N bonds in comparison to those in 1 suggests stronger conjugation between C and N atoms in the pentacene backbone of 2. The two phenyl substituents of 2 are roughly perpendicular to the pentacene plane with an angle of 85° between the ideal pentacene plane and either of the phenyl planes, and an angle of 10° between two phenyl rings. As shown in Figure 3a, the pentacene backbone of 2 is arranged cofacially but the long axes of the nearest neighboring acenes are orthogonal, resulting in a columnar cage-like supramolecular structure. The edge-to-face interactions between the phenyl substituents and the pentacene backbone are responsible for this type of molecular packing. It is found that **2** has a large  $\pi$ -to- $\pi$  distance of 4.9 Å as measured from the distance between the two central rings of neighboring molecules. In comparison to this, the (phenyl)edge-to-(pentacene)face interactions involve shorter intermolecular distances of 3.7 to 3.8 Å as measured between C atoms. The adjacent supramolecular columns of 2 contact with each other with a C-to-C distance (3.36 Å) shorter than the sum of van der Waals radii of two C atoms as shown in Figure 3b. The molecular geometry and packing motif of 2 as described above are essentially the same as those of DPP in the crystal,<sup>[15]</sup> which are shown in Figure 3c for comparison. The cage-like supramolecular structure of DPP has the same  $\pi$ -to- $\pi$  distance of 4.9 Å and similar phenyl-to-pentacene interactions with edgeto-face contacts of about 3.8 Å as measured from C to C atoms. Similar short C-to-C contacts of 3.34 Å are also found between the supramolecular columns of DPP.



**Figure 3** (a) Crystal structure of **2** showing the columnar cage-like supramolecular structure; (b) crystal structure of **2** showing the short C-to-C contacts; (c) crystal structure of DPP.<sup>[23]</sup> (C and N atoms are shown as ellipsoids at 50% probability level.)

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To contrast the isolated molecular structure with that observed in the crystal, we conducted density functional theory (DFT) calculation to optimize the molecular structures of 1 and 2 at the B3LYP level with the 6-31G(d,p) basis set. As shown in Figure 4a, energy-minimized model of 1 is very similar to its structure in the crystal having a distorted backbone bent at the N atoms with a bending angle of 139.2° between the benzene and naphthalene planes. The two phenyl groups attached to the N atoms are roughly perpendicular to each other. As shown in Figure 4b, the energy-minimized model of 2 is essentially the same as its structure in the crystal except that the model has a completely flat backbone with two phenyl groups on N atoms perpendicular to the pentacene plane. In agreement with the structures observed in the crystals, the four red C-N bonds in the model of 1 (Figure 4a) are longer than those in the model of 2 (Figure 4b) by about 0.2 Å. As calculated at the B3LYP level of DFT with the 6-311++G(d,p) basis set, the highest occupied molecular orbital (HOMO) energy levels of 1 and 2 are -5.39 eV and -4.85 eV, respectively, while the lowest unoccupied molecular orbital (LUMO) energy levels of 1 and 2 are -1.51 eV and -1.27 eV, respectively.



Figure 4 Calculated structures of 1 (a) and 2 (b).

Both **1** and **2** formed yellow solutions in  $CH_2CI_2$  exhibiting strong blue fluorescence when excited with UV light. Figure 5 shows the absorption and emission spectra of **1** and **2** as measured from their solutions in  $CH_2CI_2$  at the same concentration. **1** exhibits the longest-wavelength absorption maxima at 371 nm, which is blue shifted by 156 nm relative to that of rubrene. **2** exhibits the longest-wavelength absorption maxima at 421 nm, which is blue shifted by 177 nm relative to that of DPP. The blue-shifted absorption of **1** and **2** relative to their hydrocarbon analogues (rubrene and DPP, respectively) are similar to the absorption of **6**,13-dihydro-6,13diazapentacene, which is blue shifted relative to that of pentacene by 157 nm.<sup>[24]</sup> As found from Figure 5, **1** exhibits a Stokes shift of 102 nm, while **2** exhibits a Stokes shift of 12 nm. The much larger Stokes shift of **1** as well as its broad absorption band without fine structures can be attributed to its flexible structure, which allows the energy of the excited state to be consumed by bending the tetracene backbone and rotating the phenyl substituents on the N atoms. In contrast, the small Stocks shift of **2** suggests its pentacene backbone is rigid.



Figure 5 UV-vis absorption and fluorescence spectra of 1 and 2 in solution  $(1 \times 10^{-5} \text{ M in CH}_2\text{Cl}_2)$ . (The fluorescence spectra of 1 and 2 were recorded with excitation at 371 nm and 397 nm, respectively.)

 Table 1
 Absorption edge, oxidation potentials and energy levels of frontier

 molecular orbital for 1, 2, and their hydrocarbon analogues.

	Experimental				Calculated <sup>e</sup>	
	Optical Gap (eV) <sup>a</sup>	E <sub>ox</sub> <sup>1</sup> (V) <sup>b</sup>	HOMO (eV) <sup>c</sup>	LUMO (eV) <sup>d</sup>	HOMO (eV)	LUMO (eV)
1	2.87	0.17	-5.27	-2.40	-5.39	-1.51
2	2.83	0.14	-5.24	-2.41	-4.85	-1.27
rubrene	2.18	0.37	-5.47	-3.29	-5.03	-2.46
DPP	1.97	0.25	-5.35	-3.38	-4.84	-2.71

<sup>a</sup> Estimated from the absorption edge of the UV-vis absorption spectrum from a solution in CH<sub>2</sub>Cl<sub>2</sub> (1 × 10<sup>-5</sup> M). <sup>b</sup> Half-wave potential versus ferrocenium/ ferrocene. <sup>c</sup> Estimated from HOMO =  $-5.10 - E_{ox}^{-1}$  (eV). <sup>d</sup> Calculated from the optical gap and the HOMO energy level. <sup>e</sup> calculated at the B3LYP level of DFT with the 6-311++G(d,p) basis set.

The redox behaviours of **1** and **2** in solution were investigated with cyclic voltammetry and compared with rubrene and DPP, respectively. The cyclic voltammograms of **1**, **2** and DPP (Figure S2 in the Supporting Information) all exhibited two quasi-reversible oxidation waves, while that of rubrene exhibited one quasi-reversible oxidation wave and one irreversible oxidation wave. Based on the first oxidation potentials <sup>[25]</sup> and the absorption edges found from the UV-vis absorption spectra, the HOMO and LUMO energy levels of **1**, **2**, rubrene and DPP are estimated and summarized in Table 1. It is found that **1** and **2** have slightly higher HOMO energy levels and significantly higher LUMO energy levels than their hydrocarbon analogues (rubrene and DPP, respectively), in agreement with the fact that **1** and **2** are more electron-rich than rubrene and DPP,

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respectively. The DFT-calculated HOMO energy levels of **1** and **2** are in good agreement with the corresponding experimental values, while the calculated LUMO energy levels are higher than the corresponding experimental values by a larger degree similar to the reported N-hetero acenes.<sup>[7]</sup>

Since 1 and 2 are N-hetero analogues of rubrene and DPP, respectively, it is interesting to test whether 1 and 2 can also function as semiconductors in thin films. Therefore, thin films of 1 and 2 were deposited by thermal evaporation under a high vacuum onto silicon wafers, whose SiO<sub>2</sub> dielectric surface was pre-treated with a self-assembled monolayer (SAM) of octadecyltrimethoxysilane (OTMS). [26] The device fabrication was completed by depositing a layer of gold on the organic films through a shadow mask to form top-contact source and drain electrodes. The resulting devices had highly doped silicon as the gate electrode and a 300 nm-thick layer of SiO<sub>2</sub> as dielectrics. Not surprisingly, the films of 1 behaved as an insulator in agreement with the lack of  $\pi$ - $\pi$  interactions in the solid state. In contrast. 2 functioned as p-type semiconductors with a field effect mobility of 0.012  $\pm$  0.003 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> as measured in ambient air from at least 20 channels. The highest mobility of 2 is 0.02 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> as extracted from the transfer *I*-V curve shown in Figure 6, using the equation:  $I_{DS} = (\mu WC/2L)(V_{GS} - V_{th})^2$ , where  $I_{DS}$  is the drain current,  $\mu$  is the field-effect mobility,  $C_i$  is the capacitance per unit area for the OTMS-modified SiO<sub>2</sub> dielectric, W is the channel width, L is the channel length,  $V_{GS}$ and  $V_{th}$  are the gate and threshold voltage, respectively. The mobility of **2** is higher than the reported mobility of DPP (8×10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) in amorphous vacuum-deposited films <sup>[15]</sup> by two orders of magnitude.



**Figure 6** Drain current ( $I_{DS}$ ) versus gate voltage ( $V_{GS}$ ) with drain voltage ( $V_{DS}$ ) at -50 V for the best-performing OTFT of **2** with an active channel of W = 1 mm and  $L = 150 \,\mu$ m measured in air.

To better understand the higher field effect mobility of **2** in comparison to that of DPP, its films were investigated with X-ray diffraction (XRD) and atomic force microscope (AFM). The out-of-plane XRD patterns from the films of **2** exhibit peaks at  $2\theta = 8.00^{\circ}$  (*d* spacing of 11.05 Å),  $2\theta = 15.99^{\circ}$  (*d* spacing of 5.54 Å) and  $2\theta = 24.09^{\circ}$  (*d* spacing of 3.69 Å). These peaks correspond to (110), (220) and (330) diffractions as derived from the single crystal structure of **2**, indicating an ordered film with the (110)

lattice plane parallel to the surface. Analysis of the crystal structure reveals that molecules of 2 adopt an edge-on orientation with the pentacene plane perpendicular to the substrate surface when the (110) plane is parallel to the substrate surface. The AFM image for the film of 2 exhibits columnar crystallites in agreement with the crystalline nature of the films. Therefore the higher field effect mobility of 2 in comparison to DPP can be attributed to the higher ordering of molecules in the polycrystalline films of 2. The pathways for charge transport in the films of **2** presumably include the  $\pi$ - $\pi$ stacks within the column of **2** despite the large  $\pi$ -to- $\pi$  distance (Figure 3a) and the short C-to-C contacts between the columns (Figure 3b). However, it remains an unanswered question why 2 easily crystallizes in the vacuum-deposited films but its hydrocarbon analogue, DPP, with essentially the same molecular geometry and crystal packing cannot form crystalline films by vacuum deposition.

In summary, two novel N-phenylated N-heteroacenes 1 and 2 were synthesized and fully characterized. 1 differs from its hydrocarbon analogue, rubrene, by having a bent backbone and lacking  $\pi$ - $\pi$  interactions in the solid state. In agreement with this structure, 1 behaves as an insulator in thin films. In contrast, 2 has essentially the same molecular geometry and crystal packing as its hydrocarbon analogue, DPP. But unlike DPP, 2 crystallizes in vacuum-deposited films functioning as a p-type semiconductor with hole mobility higher than that of DPP by two orders of magnitude.

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Herein we report synthesis of two novel N-phenylated N-heteroacenes, and compare them with their hydrocarbon analogues, rubrene and 6,13-diphenylpentacene, in terms of structures and properties.



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