CHEMISTRY
A European Journal

A Journal of ChemPubSoc Europe

Accepted Article

Title: Synthesis and Properties of New N-Heteroheptacenes for Solution-Based Organic Field Effect Transistors

Authors: Fei Zhou, Sheng Liu, Bernard D. Santarsiero, Donald J. Wink, Damien Boudinet, Antonio Facchetti, and Tom G Driver

To be cited as: *Chem. Eur. J.* 10.1002/chem.201701966

Link to VoR: http://dx.doi.org/10.1002/chem.201701966

Supported by ACES

WILEY-VCH

Synthesis and Properties of New *N*-Heteroheptacenes for Solution-Based Organic Field Effect Transistors

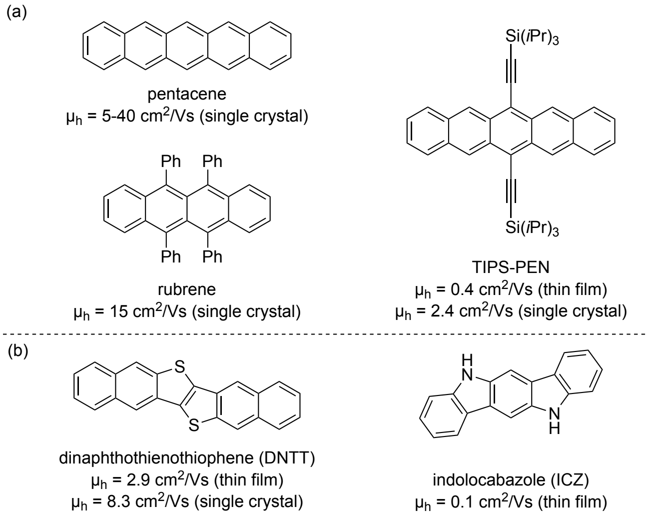
Fei Zhou,[a] Sheng Liu,[a] Bernard D. Santarsiero,[b] Donald J. Wink,[a] Damien Boudinet,[c] Antonio Facchetti,[c] and Tom Driver*[a], [d]

Abstract: A series of *N*-heteroheptacenes was synthesized from *ortho*-thiophene-substituted aryl azides using a $\mathrm{Rh_2^{II}}$-catalyzed C–H bond amination reaction to construct the thienoindole moieties. This reaction tolerated the presence of electron-donating or withdrawing groups on the aryl azide without adversely affecting the yield of the amination reaction. The central thiophene ring was created from two thienoindole pieces through a Pd-catalyzed Stille reaction to install the thioether followed by a Cu-mediated Ullman reaction to trigger the cyclization. The photophysical and electrochemical properties of the resulting focused library of *N*-heteroheptacenes revealed that the electronic nature is controlled by the arene substituent while single crystals grown reveal that the packing motif is influenced by the *N*-substituent. Solution-processed thin-film OFET devices were fabricated with the *N*-heteroheptacenes, and one exhibited a hole-mobility of 0.02 $\mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$.

Introduction

The potential optoelectronic applications of semiconducting polymers and fused-oligomeric aromatic molecules continue to inspire significant research interest because of their solution processibility and tenability.[1] Ladder-shape linear polyacenes, such as rubene, pentacene and larger acenes, have been extensively investigated because of their high carrier mobility in thin-film transistors (Figure 1a).[1f, 2] Impressive performance was achieved using pentacene and single crystal rubrene.[3] While their potential has been limited by difficult processing from solution,[4] in recent years significant strides have been made to improve their environmental stability and solubility in organic solvents.[5],[6] Thin-film transistors (FETs) based on benzo-fused heteroaromatic small molecules,[1g,7] perylenediimides[8] and diketopyrrole[9] (DPP)-based polymers have also emerged recently as alternatives because of their solubility in organic solvents facilitates solution-based processing. Devices constructed with these soluble molecules exhibit hole- and electron mobilities surpassing 5 $\mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$ and as high as 15 $\mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$.[10] Despite these advances, the synthesis of new, easily tunable organic semiconductors remain of interest in order to understand the relationship between their molecular structure and their fundamental properties and to construct solution-processed devices.

Because of their promise, significant effort has been made to develop acene- and heteroacene-based solution-processable field effect transistors. In acenes, solubilizing substituents were installed to enable the solution-based process and improve the stability against oxidation or dimerization (Scheme 1a).[11] In addition to improving the solubility, studies on these pentacene derivatives have shown the substituents also exerted significant influence on the molecular packing motif in the solid state.[12] Further, Anthony and co-workers showed that the addition of two triisopropylsilylalkynyl substituents to the central aromatic ring modified the intramolecular electronic structure and intermolecular electronic interactions.[4c,13] Placing heteroatoms into the backbone of these acenes improves their stability by lowering the HOMO energy as well as improving their solubility by enabling substitution on the heteroatoms.[2f,14] Accordingly, significant attention has been spent on thiophene-[7a,7c,15] and pyrrole-based[16] heteroacenes to produce promising materials (Scheme 1b). Heteroatom substitution in these materials produces improved secondary interactions that originate from



pentacene
μ_h = 5-40 cm^2/Vs (single crystal)

rubrene
μ_h = 15 cm^2/Vs (single crystal)

TIPS-PEN
μ_h = 0.4 cm^2/Vs (thin film)
μ_h = 2.4 cm^2/Vs (single crystal)

dinaphthothienothiophene (DNTT)
μ_h = 2.9 cm^2/Vs (thin film)
μ_h = 8.3 cm^2/Vs (single crystal)

indolocabazole (ICZ)
μ_h = 0.1 cm^2/Vs (thin film)

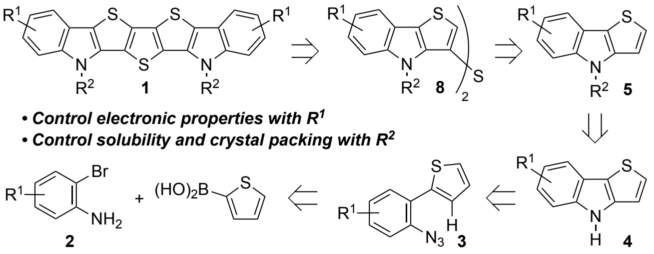
Scheme 1. Ladder-based acenes and heteroacene electronic materials.

---

[a] F. Zhou, Dr. S. Liu, Prof. Dr. D. Wink, Prof. Dr. T. Driver
Department of Chemistry
University of Illinois at Chicago
845 West Taylor Street, Chicago, IL, 60607, USA
E-mail: tgd@uic.edu
[b] Prof. Dr. B. D. Santarsiero
Center for Biomolecular Sciences
University of Illinois at Chicago
900 South Ashland Avenue, Chicago, IL, 60607, USA
[c] Dr. D. Boudinet, Dr. A. Facchetti
Flexterra Inc,
8025 Lamon Avenue, Skokie, IL, 60077, USA
[b] Prof. Dr. T. G. Driver
Institute of Next Generation Matter Transformation, College of Chemical Engineering
Huaqiao University
668 Jimei Boulevard, Chicago, Fujian, 351021, People's Republic of China

Supporting information for this article is given via a link at the end of the document.

10.1002/chem.201701966



Scheme 2. Potential synthesis of *N*-heteroacenes through Rh_2^{II}-catalyzed C–H bond amination.

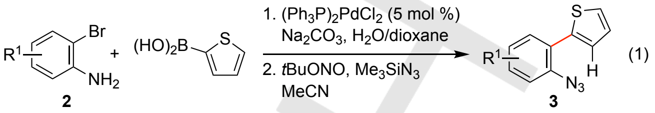
sulfur to benefit their crystal packing through hydrogen bonding and sulfur···sulfur- or sulfur···π interactions.[17] These materials have been used to construct organic field effect devices that exhibit a FET mobility up to 8.3 $cm^2 \cdot V^{-1} \cdot s^{-1}$.

N-heteroheptacenes **1** were targeted because we anticipated that their electronic- and solubility could be controlled by the choice of the indole R^1-substituent or nitrogen R^2-substituent (Scheme 2). We anticipated that these heterocycles could be assembled from two molecules of thienoindole **5** by constructing the central thiophene ring. *N*-Alkylation or *N*-arylation of **4** was envisioned to control the solubility and potentially the crystal packing of the target *N*-heteroacene. A series of thienoindoles **4** would be created from *ortho*-substituted aryl azides **3** through a Rh_2^{II}-catalyzed C–H amination reaction.[18] Our reaction would enable fine-tuning of the electronic nature of *N*-heteroheptacene **1** by varying the identity of the R^1-substituents on the arene. The requisite aryl azides would be constructed from the appropriate 2-bromoanilines **2** through a Suzuki–Miyaura cross-coupling reaction followed by an azidation reaction. If successful, this modular route would enable variation of the bulk properties of *N*-heteroacene by substituting both the nitrogen- and the indole portion.

Results and Discussion

Synthesis of N-heteroacenes

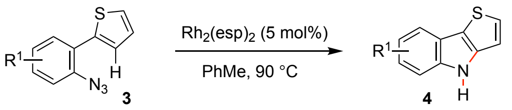
A series of *ortho*-substituted aryl azides **3** for the Rh_2^{II}-catalyzed C–H bond amination reaction were first assembled to create a focused library of *N*-heteroheptacenes (eq 1). These substrates were accessed by cross-coupling commercially available 4- and 5-substituted 2-bromoanilines **2** with thiophene boronic acid. Bromoanilines for our study were chosen to contain either electron-donating OMe-, electron-neutral H-, or electron-withdrawing F- or CF_3 R^1-substituents. At the outset of the study, we anticipated that electron-withdrawing groups would be necessary to offset inherent electron-richness of the thienoindole core. After introduction of the *ortho*-thiophene substituent using an unoptimized Suzuki–Miyaura reaction, the azide was installed using conditions reported by Moses and co-workers.[19] Submission of the anilines to *tert*-butyl nitrite and trimethylsilyl azide smoothly converted the 2-substituted anilines to the requisite aryl azides **3** for the intramolecular rhodium-catalysed *N*-heterocycle formation.

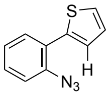
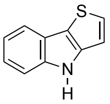
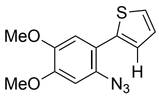
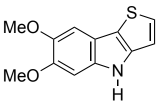
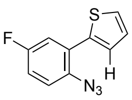
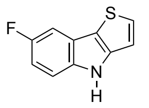
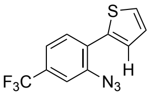
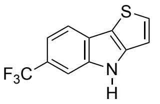


The thienoindole cores were constructed from aryl azides **3** using our Rh_2^{II}-catalysed amination reaction (Table 1).[18] After a brief survey of Rh_2^{II}-carboxylates, the best catalyst for this transformation was found to be Du Bois's $Rh_2(esp)_2$.[20] Exposure of aryl azide **3a** to this catalyst produced thienoindole **4a** in nearly quantitative yield. In contrast, thermolysis of **3a** produced the thienoindole in only 70% yield. The Rh_2^{II}-catalyzed heterocycle formation could be scaled to 5 mmol without reduction of the yield. In a similar fashion, electron-rich aryl azide **3f** or electron-deficient aryl azides **3g** and **3h** were cleanly converted to the analogous substituted thienoindoles **4f** – **4h** without any complications. We anticipated that the presence of the electron-donating or electron-withdrawing R^1-substituents on these thienoindole scaffolds would serve as a focused basis set to modulate the electronic properties of the *N*-heteroheptacene targets.

With these thienoindoles in hand, the next stage of the synthesis was to add a substituent to the nitrogen to attempt to vary the solubility and crystal-packing properties of the *N*-heteroacene targets (Table 2). To improve the solubility of the *N*-heteroacene, an *n*-dodecyl group was added (entry 1). On the

Table 1. Rh_2^{II}-Catalyzed thienoindole synthesis.



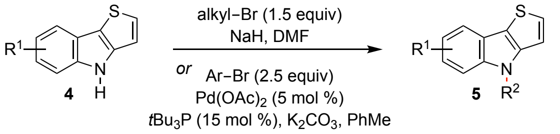
entry	#	aryl azide **3**	thienoindole **4**	yield, %[a]
1	**a**			95(70)[b]
2	**f**			82(66)[b]
3	**g**			91(68)[b]
4	**h**			75(59)[b]

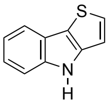
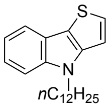
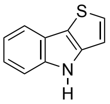
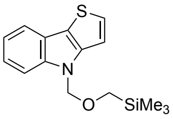
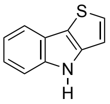
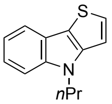
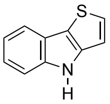
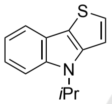
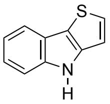
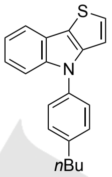
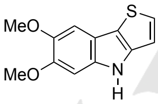
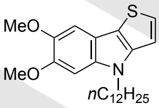
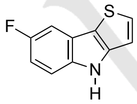
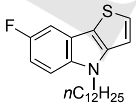
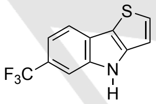
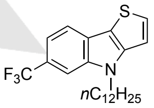
[a] Isolated after silica gel chromatography. [b] Product yield when aryl azides heated to 150 °C in xylenes for 16 h.

10.1002/chem.201701966

unsubstituted thienoindole **4a**, additional *N*-alkyl and aryl substituents were appended to determine their effect on the bulk properties of the *N*-heteroacene. A removable SEM group was attached to determine if the identity of the *N*-substituent could be modified at a late stage (entry 2). An *n*-propyl substituent was added to see if a short alkyl group would have a positive effect on the solubility of the acene (entry 3). An isopropyl substituent was installed to determine if the additional substitution on the aminomethylene might affect the crystal-packing (entry 4). Finally, an aryl substituent was added to determine if additional π-π interactions could be introduced between the stacked acenes (entry 5). To an enable comparison to **5a**, *n*-dodecyl groups were added to the unsubstituted thienoindoles **4f** – **4h** (entries 6 – 8). Together, we anticipated that these *N*-substituents would enable us to begin to develop a structure-activity relationship for the *N*-heteroacene target.

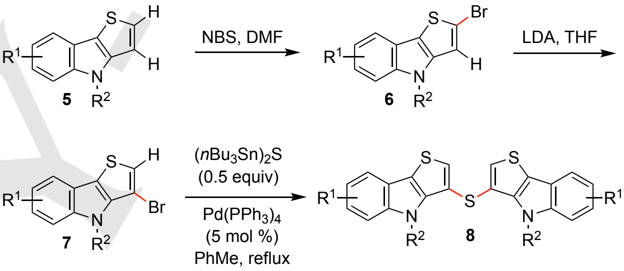
Table 2. *N*-Alkylation or *N*-arylation of thienoindole **5**.



entry	#	thienoindole **4**	thienoindole **5**	yield, %[a]
1	a			91
2	b			92
3	c			90
4	d			66
5	e			64
6	f			85
7	g			92
8	h			84

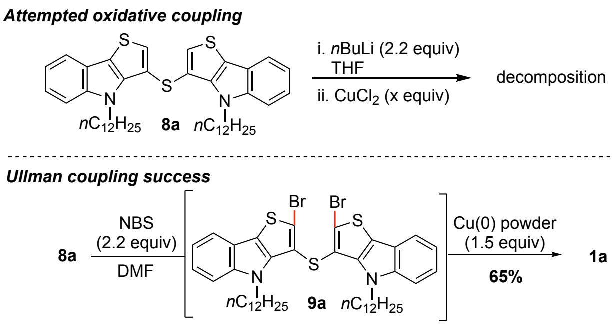
[a] Isolated after silica gel chromatography.

Next, dimerization of the thienoindoles was accomplished by installing the central thioether bond (Scheme 3). Towards this end, C2-bromination of **5** was achieved using *N*-bromosuccinimide. Following the report of Kano and co-workers,[21] an LDA-mediated "halogen-dance" isomerized **6** to the C3-brominated thienoindole **7**. The critical central thioether fragment was constructed using a Pd-catalyzed Stille reaction using the conditions reported by Kosugi and co-workers.[21b,22]



Scheme 3. Dimerization to form thioether **8**.

The final challenge was construction of the C–C bond to assemble the central thiophene ring (Scheme 4). The most common way to install this bond is through iterative deprotonation of the α-protons on the thiophene moieties followed by subsequent oxidation using CuCl$_2$.[16a, 23] This strategy, however, produced only decomposition. Optimization by varying the identity of the base, molarity or copper species did not result in a positive outcome. We attribute our negative results to the increased instability of the diionized reactive intermediate in comparison to the success cases in the literature.[24] Recently,



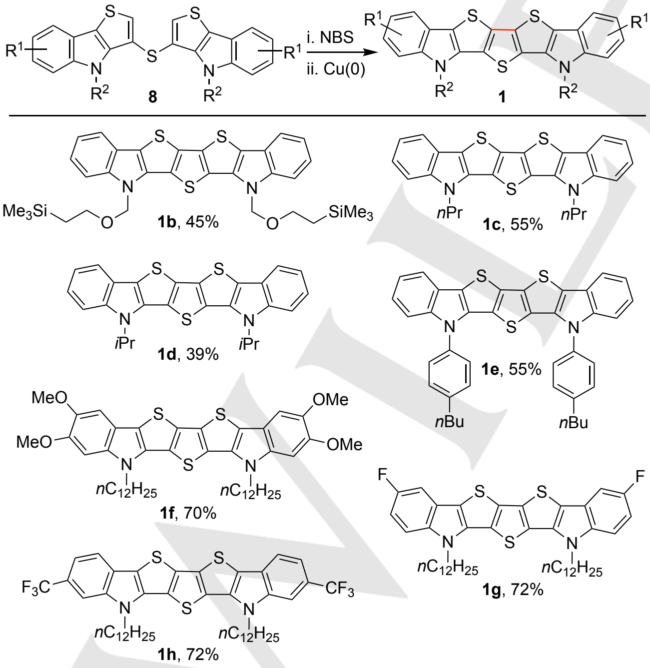
Scheme 4. Ullman Coupling to form *N*-heteroacenes.

10.1002/chem.201701966

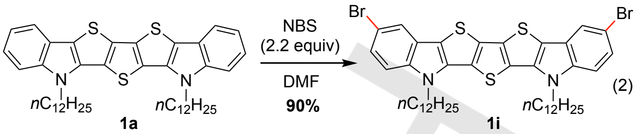
Paradies and co-workers have reported that this bond can be formed to produce a dithienothiophene through a Pd-catalyzed dihydro C–H bond coupling reaction.[25] Unfortunately, using their conditions only decomposition products were recovered. Successful formation of the central thiophene ring was only realized in our system using an Ullman coupling reaction.[26] The requisite dibromide **9** was generated *in situ* through the addition of 2.2 equivalents of *N*-bromosuccinimide in dimethylformamide.[27] After two hours, 1.5 equivalents of copper powder (+45 µm particle size) was added and the resulting mixture was heated to reflux for 16 hours to produce *N*-heteroheptacene **1a** in 65% yield from **8a**.[26],[28] Any deviation from these conditions led to a significant deleterious effect on the reaction outcome. In line with our hypothesis, bisdodecyl substituted *N*-heteroheptacene **1a** was highly soluble in organic solvents. Its solubility in toluene—a common solvent for ink jet printing—was 26 mg/mL (25 °C, 120 mg/mL at 60 °C).

Using these optimized conditions, the central thiophene ring was installed in the other thioethers **8b** – **8h** (Scheme 5). We found that changing the identity of the *N*-substituent had a detrimental effect on the yield of acene formation. In contrast, changing the electronic nature of the thienoindole had little impact on the yield of thiophene formation. Irrespective of whether an electron-donating- or electron-withdrawing substituent was present, the yield was consistently around 70%.

The solubility of *N*-heteroheptacene **1a** enabled further functionalization (eq 2). Exposure of it to an excess of *N*-bromosuccinimide smoothly produced *N*-heteroacene **1i** as a single regioisomer.[29] With a focused library of *N*- heteroheptacenes **1a** – **1i** in hand, our attention turned to examining their bulk properties in solution.



Scheme 5. Scope of Ullman coupling to form *N*-heteroheptacenes.



Solution-state properties of N-heteroacenes

Optical absorption and cyclic voltammetry measurements were performed to study the photophysical and electrochemical properties of the *N*-heteroheptacenes (Table 3, Figure 1).[30] Despite their different *N*-substituents, little variation was observed in the properties of heteroacenes **1a** – **1e** (entries 1 – 5). All systems showed similar absorption properties with a λ_{max} at 380 nm and a broad peak at approximately 390 nm (Figure 1a). Based on the similar appearance of these optical spectra to related ladder heteroacenes, the peak at 380 nm is tentatively assigned to a π-π* transition and the lower energy peak to a

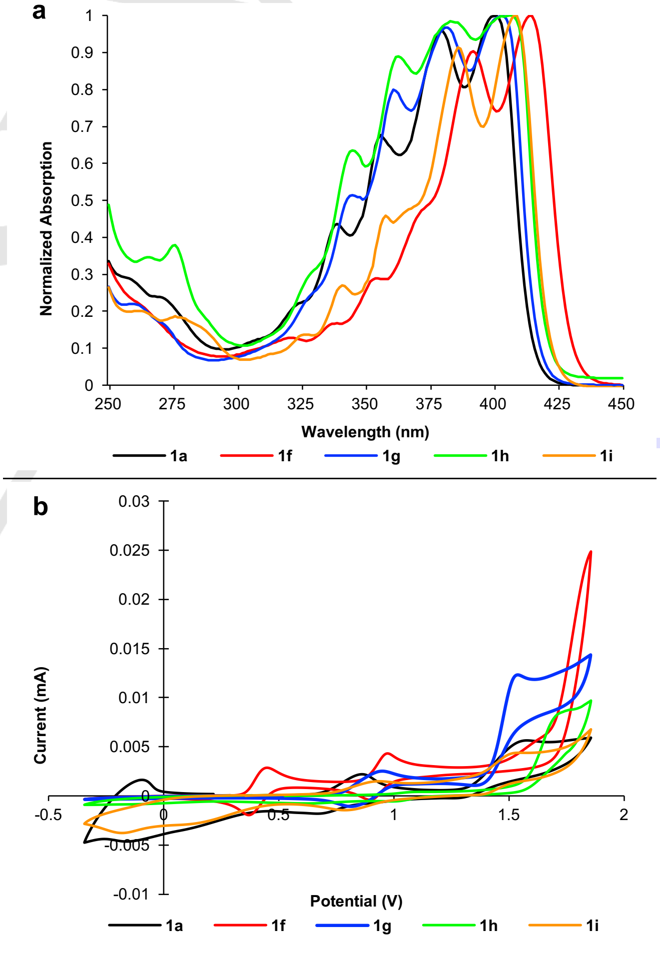


Figure 1. (a) Stacked UV-Vis spectra of 2 × 10^{-5} M solutions of *N*-heteroheptacenes **1a**, **1f**, **1g**, **1h**, and **1i** in CH_2Cl_2. (b) Stacked cyclic voltammograms of 1 × 10^{-5} M solutions of *N*-heteroheptacenes **1a**, **1f**, **1g**, **1h**, and **1i** in a 0.1 M solution of *n*-Bu_4NPF_6 in CH_2Cl_2 using a Pt working electrode with a scan rate of 50 mV·s^{-1}.

10.1002/chem.201701966

Table 3. Photophysical and electrochemical data *N*-heteroheptacenes.

entry	#	λ_{abs} (nm)^a	E_G (eV)^b	E_{ox} (V)	E_{ox}^{onset} (V)^c	E_{HOMO}^{d}	E_{LUMO}^{e}
1	**1a**	380, 401	2.92	1.00, 1.72	0.72	–5.03	–2.11
2	**1b**	377, 396	2.82	1.01, 1.66	0.79	–5.10	–2.28
3	**1c**	379, 400	2.88	0.99	0.72	–5.03	–2.15
4	**1d**	380, 401	2.90	0.99, 1.60	0.72	–5.03	–2.13
5	**1e**	379, 399	2.90	1.05	0.78	–5.09	–2.19
6	**1f**	392, 414	2.77	0.59, 1.12	0.49	–4.80	–2.13
7	**1g**	382, 403	2.88	1.09, 1.68	0.88	–5.19	–2.31
8	**1h**	383, 407	2.84	1.24	0.95	–5.26	–2.42
9	**1i**	386, 408	2.83	1.07, 1.67	0.81	–5.12	–2.29

[a] Measured in a CH_2Cl_2 solution (2×10^{-5} M). [b] Estimated from the onset of absorption [c] Potentials vs Ag/AgCl obtained from cyclic voltammetry: 0.1 M *n*-Bu_4NPF_6 in CH_2Cl_2, Pt as the working electrode with a scan rate of 50 mV·s^{-1}. The potentials are calibrated with ferrocene as the internal standard. [d] Calculated using the empirical equation $E_{HOMO} = -(E_{ox}^{onset} + 4.31)$. ^{e} Derived from E_G and E_{HOMO}.

transition that has some charge-transfer character.[31] Consequently, these *N*-heteroheptacenes all display a similar HOMO-LUMO band gap of approximately 2.90 eV. In contrast, the identity of the indole R^1-substituent exerted a much larger influence on both the photophysical and electrochemical properties of the *N*-heteroheptacene (entries 1, 6 – 9). While the trifluromethyl substituent only slightly changed the absorption peaks of **1h**, the dimethoxy substituents shifted the absorption peaks of **1f** by 12 and 13 nm. In comparison to **1a**, the dimethoxy-substituted **1h** exhibited a higher E_{HOMO} and E_{LUMO}. These higher MO energy positions suggested that it would have relatively poor aerobic stability, which was supported by the empirical observation that the color of this compound changed from yellow to black upon exposure to air. Replacing the R^1-hydrogen with an electron-withdrawing substituent lowered the E_{HOMO} and E_{LUMO} with the largest drop observed with the bistrifluoromethyl-substituted heteroacene **1h**, in which the positions of the HOMO and LUMO are lowered by approximately 0.23 and 0.31 eV. These attenuated positions manifest in the observation of only a single oxidation peak in the cyclic voltammogram. Despite this change, the band gap was hardly effected remaining in between 2.82 and 2.92 eV.

Solid-state properties of N-heteroacenes

Although the identity of the *N*-substituent did not affect the solution phase electronic nature of the *N*-heteroheptacenes, it did perturb their crystal-packing. While *N*-heteroacene **1a** proved resistant to crystallization, single crystals of **1d** and **1e** were obtained by slow evaporation from a mixture of hexanes and dichloromethane at room temperature. X-Ray crystallographic analysis revealed that both *N*-heteroheptacenes **1d** and **1e** are planar (Figure 2).[32] *N*-Isopropyl heteroheptacene **1d** packs in an

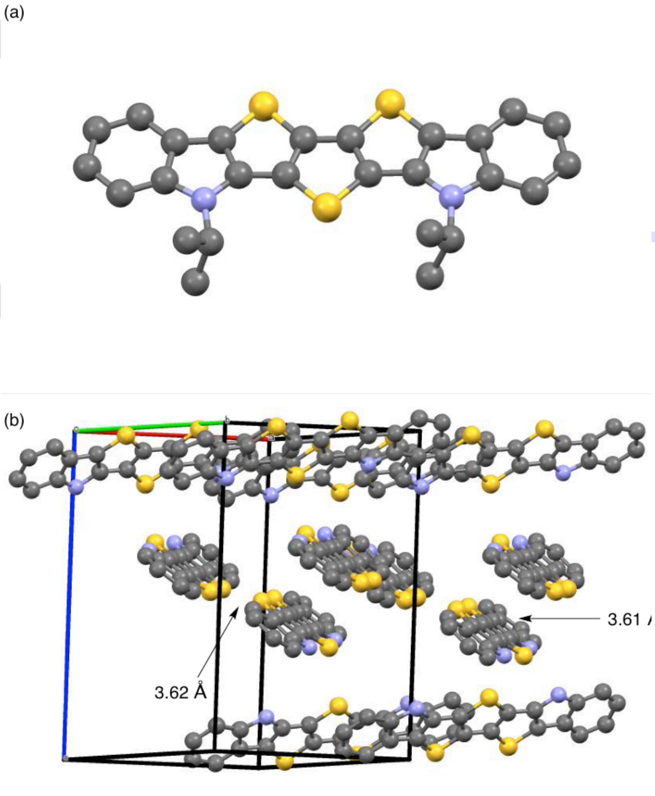


Figure 2. (a) X-Ray crystal structure of *N*-heteroheptacene **1d** (CCDC 1535577). Hydrogen atoms were removed for clarity. (b) Packing motif of *N*-heteroheptacene **1d**. Hydrogen atoms and isopropyl groups were removed for clarity.

10.1002/chem.201701966

edge-face manner,[33] which leads to a herringbone structure. To minimize the steric effect imposed by the isopropyl substituents, the antiparallel dimer was only formed with the closed C–C distance of 3.61 Å. Within one layer, the S···S interaction of 3.62 Å dominates the distance between the dimers. We attribute edge-face relationship between the layers to the C–H···π interaction of 2.80 Å between a hydrogen atom of the isopropyl group and the backbone of the adjacent molecule.[34]

In comparison to **1d**, *N*-heteroheptacene **1e** has a more complicated crystal structure (Figure 3). This increased complexity is attributed to the varying torsional angle of the *N*-4-*n*-butylphenyl-substituent with the crystal. In this crystal, two molecules form a parallel dimer to obtain a wide intermolecular π-π stacking that exhibits a closest C–C distance of 3.46 Å.[32] While one molecule shows two parallel aryl groups with a torsional angle of 51.4° and 56.2° with respect to the acene core, the other molecule's aryl groups exhibit torsional angles of 47.1° and 125.9°. This arrangement may be due to the C–H···π interaction of 3.02 Å between the hydrogen atom (H261) of the aryl group and the π-system of the aryl group in the other molecule.[34] In comparison to **1d**, the shorter distance of 3.40 – 3.42 Å between the dimers indicates that S···S interactions are more significant.[17] These interactions lead to a herringbone packing of *N*-heteroheptacene **1e**.

OFET device properties of N-heteroacenes

A series of top-gate/bottom-contact thin-film transistors (TFTs, Figure 4) were fabricated using the *N*-heteroacenes **1a** – **1g**. Top-gate bottom-contact TFTs were fabricated on poly(ethylene) naphthalate (PEN). Plastic substrates were cleaned in an ultrasound bath, and a buffer layer of ActivInk B2000 (Polyera Corporation) was spin-coated and UV-cured.[35] The gold source-drain contacts (30 nm thick) were deposited by thermal evaporation to yield channel lengths and widths of 50 µm and 1 mm, respectively. The semiconductor thin films (ca. 40 – 50 nm) were deposited on untreated Au (S-D contacts)/glass substrates by spin-coating the solutions (ca. 5 – 10 $mg\cdot mL^{-1}$). Next, the Cytop dielectric layer (~1 µM) was spin-coated from polymer solutions. After mild film annealing at 110 °C in air for 5 min, the Au-gate electrode was deposited by thermal evaporation. All the device processing and electrical measurements were performed in an ambient atmosphere, except for the Au contact vapor deposition. The field-effect mobilities µ were calculated in the saturation region by using the equation $\mu = (2I_{SD}L)/[WC_i(V_{SG} - V_{th})^2]$; where I_{SD} = saturation current, L = channel length, W = channel width, V_{SG} = gate voltage, and V_{th} = threshold voltage.

In preliminary experiments, the charge transport of these heteroacenes were investigated in a thin film transistor architecture. Among the new *N*-heteroacenes, only **1a** afforded a uniform film morphology when the semiconductor thin film was processed with dichlorobenzene as the solvent.[36] Atomic force microscopy, however, showed that this film was poorly textured (Figure 5), and an X-ray diffractogram of the film did not show any significant reflections. In contrast, the other semiconductors were rough with disconnected grains. Consequently, only semiconductor **1a** showed hole-transport mobility of 0.02 $cm^2\cdot V^{-1}\cdot s^{-1}$ with a capacitance of 2.5 $nF\cdot cm^{-2}$ and a threshold voltage of +9 V (Figure 6). This performance underscores that good transport results from the combination of a uniform film and good packing. Together with the thienoindole-based *N*-substituted heteroacenes,[37] the success of the *N*-dodecyl substituted **1a** in a thin-film field effect transistor encourages future investigation of this scaffold.

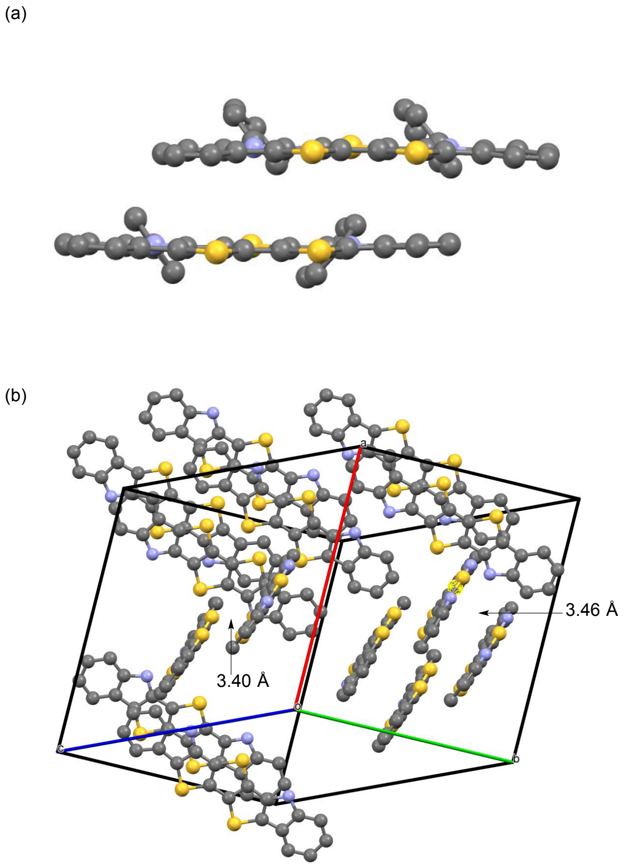


Figure 3. (a) X-Ray crystal structure of *N*-heteroheptacene **1e** (CCDC 1535588) Hydrogen atoms and *n*-butyl groups removed for clarity. (b) Packing motif of *N*-heteroheptacene **1e**. Hydrogen atoms and *n*-butylphenyl groups removed for clarity.

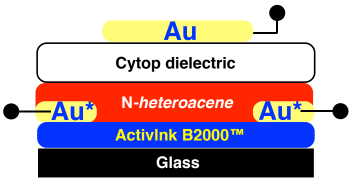


Figure 4. Structure of the bottom-contact top-gate thin film transistor used in this study.

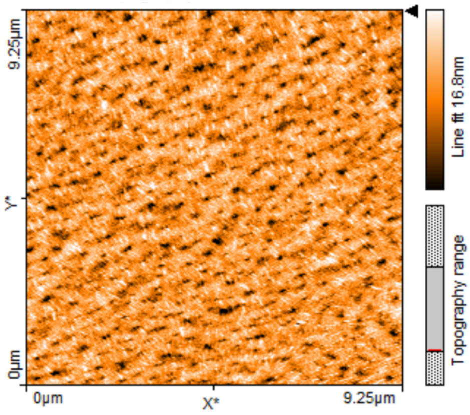


Figure 5. Atomic Force Microscopic image of a film of *N*-heteroheptacene **1a**.

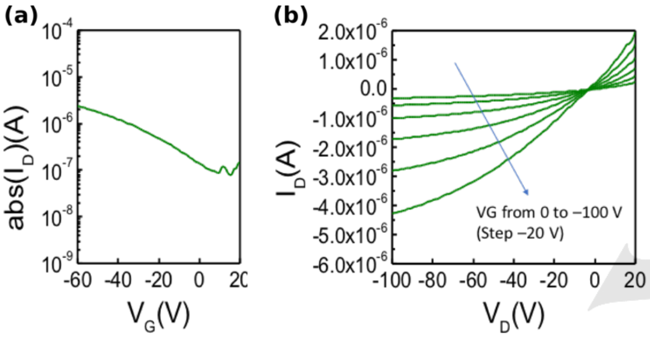


Figure 6. Field effect transistor device performance a) transfer and b) output for *N*-heteroheptacene **1a**. Saturation mobility 0.02 $cm^2 \cdot V^{-1} \cdot s^{-1}$; capacitance 2.5 $nF \cdot cm^{-2}$; W/L = 1000/50; and V_{th} = +9 V.

Conclusions

In conclusion, a focused library of *N*-heteroheptacenes were synthesized from *ortho*-thienophene substituted aryl azides using a Rh_2^{II}-catalyzed C–H bond amination reaction. The central thiophene ring was assembled from the two thienoindole pieces using palladium catalysis to install the thioether linkage followed by a Cu-mediated Ullman reaction construct the carbon–carbon bond. The photophysical and electrochemical properties of the resulting *N*-heteroheptacenes revealed that the electronic nature is controlled by the arene substituent while single-crystals grown reveal that the packing motif is influenced by the *N*-substituent. Solution-processed thin-film OFET devices were fabricated with the *N*-heteroheptacenes, and one exhibited a hole-mobility of 0.02 $cm^2 \cdot V^{-1} \cdot s^{-1}$. Future studies aimed at controlling the thin film morphology to achieve higher mobilities are currently underway.

Acknowledgments

We are grateful to the National Science Foundation (CHE-1265630), the University of Illinois at Chicago, Office of the Vice-Chancellor for Research, Huaqiao University Xiamen, and the Fujian Hundred Talents Plan for their generous financial support. AF thanks the Shenzhen Peacock Plan project (KQTD20140630110339343). We thank Mr. Furong Sun (UIUC) for high resolution mass spectrometry data.

Keywords: *N*-heteroacene • C–H bond amination • nitrene • rhodium • field effect transistor

[1] a) A. R. Murphy, J. M. J. Fréchet, *Chemical Reviews* **2007**, *107*, 1066; b) I. Osaka, R. D. McCullough, *Acc. Chem. Res.* **2008**, *41*, 1202; c) C. M. Amb, A. L. Dyer, J. R. Reynolds, *Chem. Mater.* **2010**, *23*, 397; d) P. M. Beaujuge, C. M. Amb, J. R. Reynolds, *Acc. Chem. Res.* **2010**, *43*, 1396; e) S. S. Zade, N. Zamoshchik, M. Bendikov, *Acc. Chem. Res.* **2010**, *44*, 14; f) W. Wu, Y. Liu, D. Zhu, *Chem. Soc. Rev.* **2010**, *39*, 1489; g) K. Takimiya, S. Shinamura I. Osaka, E. Miyazaki, *Adv. Mater.* **2011**, *23*, 4347; h) A. Facchetti, *Chem. Mater.* **2011**, *23*, 733; i) Y. Wen, Y. Liu, Y. Guo, G. Yu, W. Hu, *Chem. Rev.* **2011**, *111*, 3358; j) C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chemical Reviews* **2012**, *112*, 2208; k) C. Ruiz, E. M. García-Frutos, G. Hennrich, B. Gómez-Lor, *J. Phys. Chem. Lett.* **2012**, *3*, 1428; l) A. Saeki, Y. Koizumi, T. Aida, S. Seki, *Acc. Chem. Res.* **2012**, *45*, 1193; m) A. N. Sokolov, B. C. K. Tee, C. J. Bettinger, J. B. H. Tok, Z. Bao, *Acc. Chem. Res.* **2012**, *45*, 361; n) S. Kola, J. Sinha, H. E. Katz, *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 1090; o) I. McCulloch, R. S. Ashraf, L. Biniek, H. Bronstein, C. Combe, J. E. Donaghey, D. I. James, C. B. Nielsen, B. C. Schroeder, W. Zhang, *Acc. Chem. Res.* **2012**, *45*, 714; p) H. Li, G. Giri, J. B. H. Tok, Z. Bao, *MRS Bull.* **2013**, *38*, 34; q) Y. Zhao, Y. Guo, Y. Liu, *Adv. Mater.* **2013**, *25*, 5372; r) X. Guo, M. Baumgarten, K. Müllen, *Prog. Polym. Sci.* **2013**, *38*, 1832; s) S. Holliday, J. E. Donaghey, I. McCulloch, *Chem. Mater.* **2014**, *26*, 647; t) X. Gao, Y. Hu, *J. Mater. Chem. C* **2014**, *2*, 3099; u) Y. Xu, C. Liu, D. Khim, Y.-Y. Noh, *Phys. Chem. Chem. Phys.* **2015**, *17*, 26553; v) X. Guo, A. Facchetti, T. J. Marks, *Chem. Rev.* **2014**, *114*, 8943.

[2] a) M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891; b) J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028; c) J. Anthony, *Angew. Chem., Int. Ed.* **2008**, *47*, 452; d) J. Mei, Y. Diao, A. L. Appleton, L. Fang, Z. Bao, *J. Am. Chem. Soc.* **2013**, *135*, 6724; e) Q. Ye, C. Chi, *Chem. Mater.* **2014**, *26*, 4046; f) U. H. F. Bunz, *Acc. Chem. Res.* **2015**, *48*, 1676; g) K. Takimiya, M. Nakano, H. Sugino, I. Osaka, *Synth. Met.* **2016**, *217*, 68.

[3] a) O. D. Jurchescu, M. Popinciuc, B. J. van Wees, T. T. M. Palstra, *Adv. Mater.* **2007**, *19*, 688; b) Y. Takeyama, S. Ono, Y. Matsumoto, *Appl. Phys. Lett.* **2012**, *101*, 083303; c) V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, J. A. Rogers, *Science* **2004**, *303*, 1644; d) N. Stingelin-Stutzmann, E. Smits, H. Wondergem, C. Tanase, P. Blom, P. Smith, D. de Leeuw, *Nat. Mater.* **2005**, *4*, 601; e) J. Takeya, M. Yamagishi, Y. Tominari, R. Hirahara, Y. Nakazawa, T. Nishikawa, T. Kawase, T. Shimoda, S. Ogawa, *Appl. Phys. Lett.* **2007**, *90*, 102120; f) H. Tatsuo, J. Takeya, *Sci. Technol. Adv. Mater.* **2009**, *10*, 024314; g) T. Uemura, Y. Hirose, M. Uno, K. Takimiya, J. Takeya, *Appl. Phys. Express* **2009**, *2*, 111501; h) S. H. Jeong, J.-M. Choi, D. K. Hwang, S.-W. Park, S. Im, *Electrochem. Solid-State Lett.* **2007**, *10*, H321; i) F. Cicoira, J. A. Miwa, D. F. Perepichka, F. Rosei, *J. Phys. Chem. A* **2007**, *111*, 12674; j) A. S. Paraskar, A. R. Reddy, A. Patra, Y. H. Wijsboom, O. Gidron, L. J. W. Shimon, G. Leitus, M. Bendikov, *Chem. Eur. J.* **2008**, *14*, 10639.

[4] a) K. P. Weidkamp, A. Afzali, R. M. Tromp, R. J. Hamers, *J. Am. Chem. Soc.* **2004**, *126*, 12740; b) O. D. Jurchescu, J. Baas, T. T. M. Palstra, *Appl. Phys. Lett.* **2004**, *84*, 3061; c) K. P. Sung, J. E. Anthony, T. N. Jackson, *IEEE Electron Device Lett.* **2007**, *28*, 877; d) S. K. Park, T. N. Jackson, J. E. Anthony, D. A. Mourey, *Appl. Phys. Lett.* **2007**, *91*, 063514; e) L. Hung-Wei, C. Ho-Jung, L. Guann-Pyng, M. Bachman, *IEEE Electron Device Lett.* **2009**, *30*, 346.

[5] a) K. A. McGarry, W. Xie, C. Sutton, C. Risko, Y. Wu, V. G. Young, J.-L. Brédas, C. D. Frisbie, C. J. Douglas, *Chem. Mater.* **2013**, *25*, 2254; b) W. Xie, K. A. McGarry, F. Liu, Y. Wu, P. P. Ruden, C. J. Douglas, C. D. Frisbie, *J. Phys. Chem. C* **2013**, *117*, 11522; c) W. Xie, P. L. Prabhumirashi, Y. Nakayama, K. A. McGarry, M. L. Geier, Y. Uragami, K. Mase, C. J. Douglas H. Ishii, M. C. Hersam, C. D. Frisbie, *ACS Nano* **2013**, *7*, 10245; d) T. K. Mullenbach, K. A. McGarry, W. A. Luhman, C. J. Douglas, R. J. Holmes, *Adv. Mater.* **2013**, *25*, 3689; e) P. S. Jo, D. T. Duong, J. Park, R. Sinclair, A. Salleo, *Chem. Mater.* **2015**, *27*, 3979; f) X. Hu, Z. Wang, X. Zhu, T. Zhu, X. Zhang, B. Dong, L. Huang, L. Chi, *Small* **2016**, *12*, 4086.

[6] a) D. H. Kim, D. Y. Lee, S. G. Lee, K. Cho, *Chem. Mater.* **2012**, *24*, 2752; b) O. L. Griffith, J. E. Anthony, A. G. Jones, Y. Shu, D. L. Lichtenberger, *J. Am. Chem. Soc.* **2012**, *134*, 14185; c) S. M. Ryno, C. Risko, J.-L. Brédas, *J. Am. Chem. Soc.* **2014**, *136*, 6421; d) E. T. Chernick, R. Casillas, J. Zirzlmeier, D. M. Gardner, M. Gruber, H. Kropp, K. Meyer, M. R. Wasielewski, D. M. Guldi, R. R. Tykwinski, *J. Am. Chem. Soc.* **2015**, *137*, 857; e) G. Oh, J.-S. Kim, J. H. Jeon, E. Won, J. W. Son, D. H. Lee, C. K.

Kim, J. Jang, T. Lee, B. H. Park, *ACS Nano* **2015**, *9*, 7515; f) C.-H. Kim, H. Hlaing, M. M. Payne, S. R. Parkin, J. E. Anthony, I. Kymissis, *Chemphyschem* **2015**, *16*, 1251; g) K. Kim, E. J. G. Santos, T. H. Lee, Y. Nishi, Z. Bao, *Small* **2015**, *11*, 2037.

[7] a) T. Yamamoto, K. Takimiya, *J. Am. Chem. Soc.* **2007**, *129*, 2224; b) H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, T. Yui, *J. Am. Chem. Soc.* **2007**, *129*, 15732; c) K. Niimi, S. Shinamura, I. Osaka, E. Miyazaki, K. Takimiya, *J. Am. Chem. Soc.* **2011**, *133*, 8732; d) T. V. Pho, J. D. Yuen, J. A. Kurzman, B. G. Smith, M. Miao, W. T. Walker, R. Seshadri, F. Wudl, *J. Am. Chem. Soc.* **2012**, *134*, 18185.

[8] a) B. A. Gregg, R. A. Cormier, *J. Am. Chem. Soc.* **2001**, *123*, 7959; b) R. T. Weitz, K. Amsharov, U. Zschieschang, E. B. Villas, D. K. Goswami, M. Burghard, H. Dosch, M. Jansen, K. Kern, H. Klauk, *J. Am. Chem. Soc.* **2008**, *130*, 4637; c) E. Zhou, J. Cong, Q. Wei, K. Tajima, C. Yang, K. Hashimoto, *Angew. Chem. Int. Ed.* **2011**, *50*, 2799; d) X. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, S. R. Marder, *Adv. Mater.* **2011**, *23*, 268.

[9] a) B. Tieke, A. R. Rabindranath, K. Zhang, Y. Zhu, *Beilstein J Org Chem* **2010**, *6*, 830; b) Y. Li, P. Sonar, S. P. Singh, M. S. Soh, M. van Meurs, J. Tan, *J. Am. Chem. Soc.* **2011**, *133*, 2198; c) J. S. Ha, K. H. Kim, D. H. Choi, *J. Am. Chem. Soc.* **2011**, *133*, 10364; d) Z. Chen, M. J. Lee, R. Shahid Ashraf, Y. Gu, S. Albert-Seifried, M. Meedom Nielsen, B. Schroeder, T. D. Anthopoulos, M. Heeney, I. McCulloch, H. Sirringhaus, *Adv. Mater.* **2012**, *24*, 647; e) J. S. Lee, S. K. Son, S. Song, H. Kim, D. R. Lee, K. Kim, M. J. Ko, D. H. Choi, B. Kim, J. H. Cho, *Chem. Mater.* **2012**, *24*, 1316; f) H. Chen, Y. Guo, G. Yu, Y. Zhao, J. Zhang, D. Gao, H. Liu, Y. Liu, *Adv. Mater.* **2012**, *24*, 4618; g) C. Kanimozhi, N. Yaacobi-Gross, K. W. Chou, A. Amassian, T. D. Anthopoulos, S. Patil, *J. Am. Chem. Soc.* **2012**, *134*, 16532; h) S. Qu, H. Tian, *Chem. Commun.* **2012**, *48*, 3039; i) C. B. Nielsen, M. Turbiez, I. McCulloch, *Adv. Mater.* **2013**, *25*, 1859; j) W. Li, K. H. Hendriks, M. M. Wienk, R. A. J. Janssen, *Acc. Chem. Res.* **2016**, *49*, 78.

[10] H. Minemawari, T. Yamada, H. Matsui, J. y. Tsutsumi, S. Haas, R. Chiba, R. Kumai, T. Hasegawa, *Nature* **2011**, *475*, 364.

[11] a) J. E. Anthony, D. L. Eaton, S. R. Parkin, *Org. Lett.* **2001**, *4*, 15; b) J. E. Anthony, J. Gierschner, C. A. Landis, S. R. Parkin, J. B. Sherman, R. C. Bakus Ii, *Chem. Commun.* **2007**, 4746; c) M. M. Payne, S. R. Parkin, J. E. Anthony, *J. Am. Chem. Soc.* **2005**, *127*, 8028; d) M. M. Payne, S. R. Parkin, J. E. Anthony, C.-C. Kuo, T. N. Jackson, *J. Am. Chem. Soc.* **2005**, *127*, 4986.

[12] a) J. E. Anthony, J. S. Brooks, D. L. Eaton, S. R. Parkin, *J. Am. Chem. Soc.* **2001**, *123*, 9482; b) C. D. Sheraw, T. N. Jackson, D. L. Eaton, J. E. Anthony, *Adv. Mater.* **2003**, *15*, 2009; c) H. Li, B. C. Tee, G. Giri, J. W. Chung, S. Y. Lee, Z. Bao, *Adv. Mater.* **2012**, *24*, 2588; d) K. J. Thorley, T. W. Finn, K. Jarolimek, J. E. Anthony, C. Risko, *Chem. Mater.* **2016**, doi: 10.1021/acs.chemmater.6b04211.

[13] a) A. Troisi, G. Orlandi, J. E. Anthony, *Chem. Mater.* **2005**, *17*, 5024; b) H. Y. Chen, I. Chao, *Chemphyschem* **2006**, *7*, 2003; c) G. Lobanova, Olga, N. E. Gruhn, J. E. Anthony, B. Purushothaman, D. L. Lichtenberger, *J. Phys. Chem. C* **2008**, *112*, 20518; d) O. L. Griffith, J. E. Anthony, A. G. Jones, D. L. Lichtenberger, *J. Am. Chem. Soc.* **2010**, *132*, 580.

[14] a) U. H. F. Bunz, J. U. Engelhart, *Chem. Eur. J.* **2016**, *22*, 4680; b) J. U. Engelhart, F. Paulus, M. Schaffroth, V. Vasilenko, O. Tverskoy, F. Rominger, U. H. F. Bunz, *J. Org. Chem.* **2016**, *81*, 1198; c) S. Hahn, F. L. Geyer, S. Koser, O. Tverskoy, F. Rominger, U. H. F. Bunz, *J. Org. Chem.* **2016**, *81*, 8485.

[15] a) X. Zhang, J. P. Johnson, J. W. Kampf, A. J. Matzger, *Chem. Mater.* **2006**, *18*, 3470; b) E.-G. Kim, V. Coropceanu, N. E. Gruhn, R. S. Sánchez-Carrera, R. Snoeberger, A. J. Matzger, J.-L. Brédas, *J. Am. Chem. Soc.* **2007**, *129*, 13072; c) J.-I. Park, J. W. Chung, J.-Y. Kim, J. Lee, J. Y. Jung, B. Koo, B.-L. Lee, S. W. Lee, Y. W. Jin, S. Y. Lee, *J. Am. Chem. Soc.* **2015**, *137*, 12175; d) U. Kraft, J. E. Anthony, E. Ripaud, M. A. Loth, E. Weber, H. Klauk, *Chem. Mater.* **2015**, *27*, 998; e) T. Zheng, Z. Cai, R. Ho-Wu, S. H. Yau, V. Shaparov, T. Goodson, L. Yu, *J. Am. Chem. Soc.* **2016**, *138*, 868; f) K. J. Thorley, C. Risko, *J. Mater. Chem. C* **2016**, *4*, 4040.

[16] a) T. Qi, W. Qiu, Y. Liu, H. Zhang, X. Gao, Y. Liu, K. Lu, C. Du, G. Yu, D. Zhu, *J. Org. Chem.* **2008**, *73*, 4638; b) P. Gao, X. Feng, X. Yang, V. Enkelmann, M. Baumgarten, K. Müllen, *J. Org. Chem.* **2008**, *73*, 9207; c) H. Zhao, L. Jiang, H. Dong, H. Li, W. Hu, B. S. Ong, *Chemphyschem* **2009**, *10*, 2345; d) C. Wetzel, E. Brier, A. Vogt, A. Mishra, E. Mena-Osteritz, P. Bäuerle, *Angew. Chem. Int. Ed.* **2015**, *54*, 12334; e) I. Cho, N. J. Jeon, O. K. Kwon, D. W. Kim, E. H. Jung, J. H. Noh, J. Seo, S. I. Seok, S. Y. Park, *Chem. Sci.* **2017**, *8*, 734.

[17] a) K. Xiao, Y. Liu, T. Qi, W. Zhang, F. Wang, J. Gao, W. Qiu, Y. Ma, G. Cui, S. Chen, X. Zhan, G. Yu, J. Qin, W. Hu, D. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 13281; b) T. Izawa, E. Miyazaki, K. Takimiya, *Adv. Mater.* **2008**, *20*, 3388; c) N. E. Jackson, B. M. Savoie, K. L. Kohlstedt, M. Olvera de la Cruz, G. C. Schatz, L. X. Chen, M. A. Ratner, *J. Am. Chem. Soc.* **2013**, *135*, 10475; d) W. Yi, S. Zhao, H. Sun, Y. Kan, J. Shi, S. Wan, C. Li, H. Wang, *J. Mater. Chem. C* **2015**, *3*, 10856; e) C. Sutton, C. Risko, J.-L. Brédas, *Chem. Mater.* **2016**, *28*, 3; f) G. Conboy, H. J. Spencer, E. Angioni, A. L. Kanibolotsky, N. J. Findlay, S. J. Coles, C. Wilson, M. B. Pitak, C. Risko, V. Coropceanu, J.-L. Bredas, P. J. Skabara, *Mater. Horiz.* **2016**, *3*, 333.

[18] a) M. Shen, B. E. Leslie, T. G. Driver, *Angew. Chem. Int. Ed.* **2008**, *47*, 5056; b) H. Dong, R. T. Latka, T. G. Driver, *Org. Lett.* **2011**, *13*, 2726; c) A. L. Pumphrey, H. Dong, T. G. Driver, *Angew. Chem. Int. Ed.* **2012**, *51*, 5920; d) N. Jana, Q. Nguyen, T. G. Driver, *J. Org. Chem.* **2014**, *79*, 2781; e) C. Kong, N. Jana, C. Jones, T. G. Driver, *J. Am. Chem. Soc.* **2016**, *138*, 13271.

[19] a) K. Barral, A. D. Moorhouse, J. E. Moses, *Org. Lett.* **2007**, *9*, 1809; b) F. Zhang, J. E. Moses, *Org. Lett.* **2009**, *11*, 1587.

[20] a) C. G. Espino, K. W. Fiori, M. Kim, J. Du Bois, *J. Am. Chem. Soc.* **2004**, *126*, 15378; b) D. N. Zalatan, J. Du Bois, *J. Am. Chem. Soc.* **2009**, *131*, 7558.

[21] a) S. Kano, Y. Yuasa, T. Yokomatsu, S. Shibuya, *Heterocycles* **1983**, *20*, 2035; b) X. Zhang, A. P. Côté, A. J. Matzger, *J. Am. Chem. Soc.* **2005**, *127*, 10502.

[22] M. Kosugi, T. Ogata, M. Terada, H. Sano, T. Migita, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3657.

[23] F. Allared, J. Hellberg, T. Remonen, *Tetrahedron Lett.* **2002**, *43*, 1553.

[24] a) Y. Mazaki, K. Kobayashi, *Tetrahedron Lett.* **1989**, *30*, 3315; b) G. Barbarella, L. Favaretto, G. Sotgiu, L. Antolini, G. Gigli, R. Cingolani, A. Bongini, *Chem. Mater.* **2001**, *13*, 4112; c) M. He, F. Zhang, *J. Org. Chem.* **2007**, *72*, 442; d) M. San, Lidaris, W. W. Porter, III, A. J. Matzger, *Org. Lett.* **2007**, *9*, 1005; e) J. T. Henssler, X. Zhang, A. J. Matzger, *J. Org. Chem.* **2009**, *74*, 9112; f) I. Palamà, F. Di Maria, I. Viola, E. Fabiano, G. Gigli, C. Bettini, G. Barbarella, *J. Am. Chem. Soc.* **2011**, *133*, 17777; g) S.-Y. Ku, C. D. Liman, D. J. Burke, N. D. Treat, J. E. Cochran, E. Amir, L. A. Perez, M. L. Chabinyc, C. J. Hawker, *Macromolecules* **2011**, *44*, 9533; h) P. He, Z. Tu, G. Zhao, Y. Zhen, H. Geng, Y. Yi, Z. Wang, H. Zhang, C. Xu, J. Liu, X. Lu, X. Fu, Q. Zhao, X. Zhang, D. Ji, L. Jiang, H. Dong, W. Hu, *Adv. Mater.* **2015**, *27*, 825; i) K. Moriya, D. Didier, M. Simon, J. M. Hammann, G. Berionni, K. Karaghiosoff, H. Zipse, H. Mayr, P. Knochel, *Angew. Chem. Int. Ed.* **2015**, *54*, 2754.

[25] P. Oechsle, J. Paradies, *Org. Lett.* **2014**, *16*, 4086.

[26] K. Ogawa, S. C. Rasmussen, *J. Org. Chem.* **2003**, *68*, 2921.

[27] a) K. Tamao, S. Kodama, I. Nakajima, M. Kumada, A. Minato, K. Suzuki, *Tetrahedron* **1982**, *38*, 3347; b) M. J. Marsella, R. J. Reid, *Macromolecules* **1999**, *32*, 5982; c) M. J. Marsella, G. Piao, F. S. Tham, *Synthesis* **2002**, 1133; d) K.-H. Lee, J. Ohshita, A. Kunai, *Organometallics* **2004**, *23*, 5365.

[28] a) H.-L. Wong, C.-C. Ko, W. H. Lam, N. Zhu, V. W.-W. Yam, *Chem. Eur. J.* **2009**, *15*, 10005; b) J. C. Bijleveld, M. Shahid, J. Gilot, M. M. Wienk, R. A. J. Janssen, *Adv. Funct. Mater.* **2009**, *19*, 3262; c) H. Hanamura, R. Haneishi, N. Nemoto, *Tetrahedron Lett.* **2011**, *52*, 4039.

[29] a) G. Buchmann, D. Rossner, *J. Prakt. Chem.* **1964**, *25*, 117; b) R. M. Acheson, R. J. Prince, G. Procter, *J. Chem. Soc., Perkin Trans. 1* **1979**, 595; c) M. L. Trudell, S. L. Lifer, Y. C. Tan, W. B. England, J. M. Cook, *J. Org. Chem.* **1988**, *53*, 4185.

[30] For a detailed experimental procedure and individual spectra for each of the *N*-heteroheptacenes **1a** – **1i**, please refer to the Supporting Information.

[31] a) R. M. Walczak, J. R. Reynolds, *Adv. Mat.* **2006**, *18*, 1121; b) S. C. Rasmussen, D. J. Sattler, K. A. Mitchell, J. Maxwell, *J. Lumin.* **2004**, *109*, 111; c) L. Wen, J. P. Nietfeld, C. M. Amb, S. C. Rasmussen, *J. Org. Chem.* **2008**, *73*, 8529; d) J. P. Wagner, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2015**, *54*, 12274.

[32] a) S. Grimme, *Angew. Chem. Int. Ed.* **2008**, *47*, 3430; b) S. E. Wheeler, K. N. Houk, *J. Am. Chem. Soc.* **2008**, *130*, 10854; c) Y. Geng, T. Takatani, E. G. Hohenstein, C. D. Sherrill, *J. Phys. Chem. A* **2010**, *114*, 3576; d) S. E. Wheeler, *J. Am. Chem. Soc.* **2011**, *133*, 10262.

[33] a) M. O. Sinnokrot, C. D. Sherrill, *J. Phys. Chem. A* **2004**, *108*, 10200; b) E. C. Lee, B. H. Hong, J. Y. Lee, J. C. Kim, D. Kim, Y. Kim, P. Tarakeshwar, K. S. Kim, *J. Am. Chem. Soc.* **2005**, *127*, 4530; c) A. L. Ringer, M. O. Sinnokrot, R. P. Lively, C. D. Sherrill, *Chem. Eur. J.* **2006**, *12*, 3821; d) R. Podeszwa, K. Szalewicz, *Phys. Chem. Chem. Phys.* **2008**, *10*, 2735.

[34] a) S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, K. Tanabe, *J. Am. Chem. Soc.* **2000**, *122*, 3746; b) M. Nishio, *CrystEngComm* **2004**, *6*, 130; c) S. Tsuzuki, K. Honda, A. Fujii, T. Uchimaru, M. Mikami, *Phys. Chem. Chem. Phys.* **2008**, *10*, 2860; d) M. Saggu, N. M. Levinson, S. G. Boxer, *J. Am. Chem. Soc.* **2012**, *134*, 18986; e) S. Karthikeyan, V. Ramanathan, B. K. Mishra, *J. Phys. Chem. A* **2013**, *117*, 6687.

[35] ActivInk is a photocurable polymer material commercially available from Polyera Corporation, see: A. Facchetti, Z. Chen, H. Yan, Y. Zheng, J. Quinn M. Kastler, F. Dötz, S. Koehler, Naphthalene-imide semiconductor polymers WO2009098253, Oct 15, 2009.

[36] J.-F. Chang, B. Sun, D. W. Breiby, M. M. Nielsen, T. I. Sölling, M. Giles, I. McCulloch, H. Sirringhaus, *Chem. Mater.* **2004**, *16*, 4772.

[37] a) T. Qi, Y. Guo, Y. Liu, H. Xi, H. Zhang, X. Gao, Y. Liu, K. Lu, C. Du, G. Yu, D. Zhu, *Chem. Commun.* **2008**, 6227; b) G. Balaji, S. Valiyaveettil, *Org. Lett.* **2009**, *11*, 3358; c) G. Balaji, A. M. Della Pelle, B. C. Popere, A. Chandrasekaran, S. Thayumanavan, *Org. Biomol. Chem.* **2012**, *10*, 3455; d) S.-i. Kato, T. Furuya, A. Kobayashi, M. Nitani, Y. Ie, Y. Aso, T. Yoshihara, S. Tobita, Y. Nakamura, *J. Org. Chem.* **2012**, *77*, 7595.

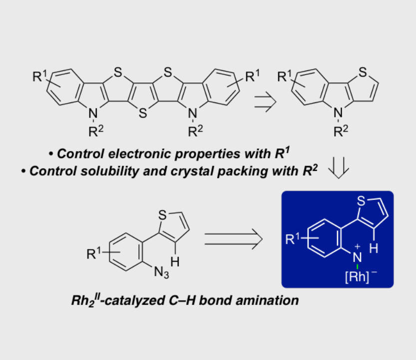
10.1002/chem.201701966

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

A series of *N*-heteroheptacenes was synthesized from *ortho*-thiophene-substituted aryl azides using a Rh_2^{II}-catalyzed C–H bond amination reaction. The solution- and solid-state properties are reported.



*F. Zhou, S. Liu, B. D. Santarsiero, D. J. Wink, D. Boudinet, A. Facchetti and T. G. Driver**

Page No. – Page No.

Synthesis and Properties of New *N*-Heteroheptacenes for Solution-Based Organic Field Effect Transistors

Layout 2:

FULL PAPER

((Insert TOC Graphic here; max. width: 11.5 cm; max. height: 2.5 cm))

*Author(s), Corresponding Author(s)**

Page No. – Page No.

Title

Text for Table of Contents