JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Synthesis and Physical Properties of Four Hexazapentacene Derivatives

Gang Li,[†,‡] Yuechao Wu,[†,‡] Junkuo Gao,[†] Chengyuan Wang,[†] Junbo Li,[†] Huacheng Zhang,[§] Yang Zhao,[†] Yanli Zhao,[§] and Qichun Zhang*[,†]

[†]School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

[§]Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

Supporting Information

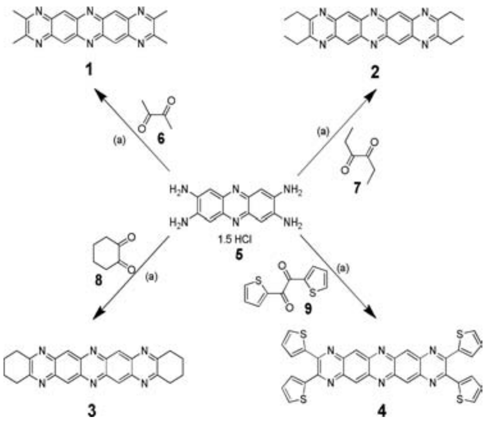
ABSTRACT: In two steps from commercially available starting materials, four novel hexazapentacene derivatives have been synthesized through cyclocondensation reaction between tetraamines and 1,2-diketones. The observed optical bandgaps for 2,3,9,10-tetramethyl-1,4,6,8,11,13-hexaza-pentacene (**TMHAP**, **1**), tetraethyl-1,4,6,8,11,13-hexaza-pentacene (**TEHAP**, **2**), 1,2,3,4,10,11,12,13-octahydro-5,7, 9,14,16,18-hexazaheptacene (**OHHAH**, **3**), and tetra(2-thioyl)-1,4,6,8,11,13-hexazapentacene (**TTHAP**, **4**) are 2.55, 2.55, 2.45, and 2.25 eV, respectively. The cyclic voltammetry measurements show that all compounds exhibit one revisable reduction waves. The calculated bandgaps through DFT calculations for **TMHAP** (**1**), **TEHAP** (**2**), **OHAH** (**3**), and **TTHAP** (**4**) are 2.41, 2.41, 2.34, and 2.15 eV, respectivly, which are close to the experimental results. Our success in synthesizing hexazapentacene derivatives might offer a promising strategy to challenge larger azaacenes with more N atoms.

In past decades, there has been significant interest in developing larger acenes[1−3] because of their potential applications in semiconducting devices such as organic field effect transistors (OFETs),[3a,4] organic light-emitting diodes (OLEDs),[5] and photovoltaic cells.[6] However, without any exception, the parent acenes always display p-type characteristics and the hole mobility of thin films can go as high as 4.28 cm^2 V^{-1} s^{-1}.[3a] As the counterparts, n-type materials, which are the required active materials in semiconducting devices to complete p−n junctions or complementary logic behaviors, are obviously lagged.[7] Currently, pursuing high-performance n-type materials has become the focus of materials research. One strategy suggested by Houk et al. is that N-substituted acenes could exhibit promising electron-transport behaviors because of their high electron affinities.[8] Moreover, N-substituted acenes are believed to be less sensitive to degradation through oxidation or dimerization.[9] Furthermore, the number, position, and valence states of N atoms in backbones make the properties of N-substituted acenes more diverse.[8,10] All these exciting features highlight the resurgence of research on N-substituted acenes.

Because of their strongly enhanced electron affinities, *N*-heteroacenes as n-channel organic semiconductors have been widely observed.[11,12] Some of them have already shown reasonable electron mobilities. More importantly, the replacement of CH groups with sp^2 N atoms will offer many chances to manipulate stability, photophysical and electrical properties, and diverse structural backbones of *N*-heteroacenes. To fully understand the structure/property relationship, it is necessary to prepare more novel *N*-heteroacenes to enrich this family.

There are two convenient methods to create *N*-heteroacenes:[13] (a) condensation reactions between *ortho*-diaminoacenes and *ortho*-diketoacene (or hydroxyl-ketone) and (b) substituted reactions between *ortho*-diaminoacenes and *ortho*-dihydroxylacenes (or *ortho*-dihaloacenes or *ortho*-dicyanoacenes) following oxidation. In our research, we are more interested in the first method because the formation of C═N bonds can be readily achieved through simple cyclocondension reaction from commercially available reagents or easily prepared immediates. Here, we reported the synthesis, characterization, and properties of four novel N-substituted pentacenes (Scheme 1): 2,3,9,10-tetramethyl-1,4,6,8,11,13-hexazapentacene (**TMHAP**, **1**), tetraethyl-1,4,6,8,11,13-hexazapentacene (**TEHAP**, **2**), 1,2,3,4,10,11,12,13-octahydro-

Scheme 1. Synthetic Route of Four Hexazapentacene Derivatives: TMHAP (1), TEHAP (2), OHAH (3), and TTHAP (4)[a]



[a]Reaction condition: (a) acetic acid, IBX, reflux, 48 h.

Received: October 17, 2012
Published: December 6, 2012

dx.doi.org/10.1021/ja310131k | J. Am. Chem. Soc. 2012, 134, 20298−20301

5,7,9,14,16,18-hexazaheptacene (**OHHAH**, **3**), and tetra(2-thioyl)-1,4,6,8,11,13-hexazapentacene (**TTHAP**, **4**).

Four novel hexazapentacene derivatives **1−4** were successfully synthesized through the cyclocondensation reaction between 9,10-diazo-2,3,6,7-tetraaminoanthrance hydrochloride salt (**5**)[14] and the corresponding commercially available diketones **6−9** (Scheme 1). All as-prepared compounds **TMHAP** (**1**), **TEHAP** (**2**), **OHHAH** (**3**), and **TTHAP** (**4**) have been fully characterized by elemental analysis, ^{1}H NMR, FT-IR, and high-resolution mass spectrometry. Because of their poor solubility, we only observed the ^{13}CNMR spectrum of **TTHAP** (**4**) (see Supporting Information).

The ^{1}HNMR spectra (in CF_3COOD, 400 MHz) of four hexazapentacene derivatives **1−4** are shown in Figure 1. The aromatic proton signal at 7.49 ppm (s, 4H) in Figure 1a belongs to H-a in **TMHAP** (**1**). The proton signal for methyl group in **TMHAP** (**1**) can be observed at 2.79 ppm (s, 12H). Compared to compound **1**, the aromatic proton signals of **TEHAP** (**2**, 7.59 ppm, 4H) and **OHHAH** (**3**, 7.70 ppm, 4H) are shifted to relatively lower field. The peaks at 1.48 ppm (t, 12H) and 3.15 ppm (q, 8H) in Figure 2b can be assigned to the protons in ethyl group of **TEHAP** (**2**) while two triplet signals (3.27 ppm (8H) and 2.16 ppm (8H)) in Figure 1c are contributed from the protons in cyclohexane groups of **OHHAH** (**3**). Since **TTHAP** (**4**) has no alkane groups, all proton peaks are observed in lower field. Clearly, the peaks at 7.88 ppm (d, 4H), 7.72 ppm (d, 4H), 7.30 ppm (q, 4H) belong to the protons in thiophene group, namely, H-d, H-b, and H-c, respectively, and the single peak at 7.79 ppm (4H) comes from the protons in hexazapentacene backbone.

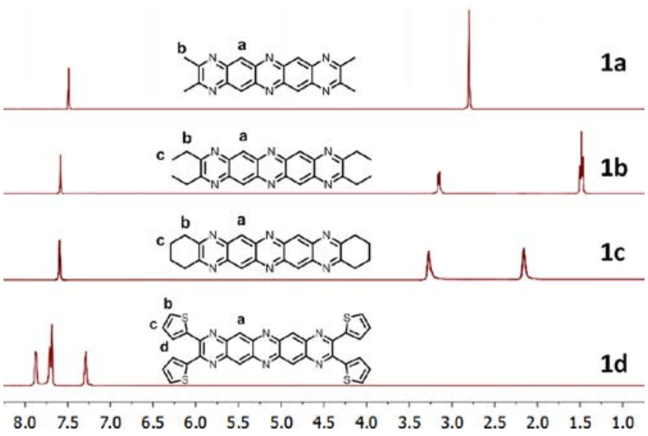


Figure 1. ^{1}H NMR spectra of hexazapentacene derivatives **1−4** in TFA-*d* solutions.

Using dimethylformamide (DMF) as solvent, **TMHAP** (**1**) and **TEHAP** (**2**) form orange solutions, while **OHHAH** (**3**) gives a pink solution and **TTHAP** (**4**) generates a red color (Figure 2a, inset). The phenomena come from two aspects: (1) the effect of substituted groups and (2) solvent effect. For **TTHAP** (**4**), there might be some intramolecular charge transfer between thiophene groups and hexazapentacene backbone, which will cause the red-shifted UV−vis absorption (Figure 2a). As to **OHHAH** (**3**), the tailed, red-shifted UV−vis absorption might come from synergistic effects resulting from cyclohexane groups and DMF molecules. It is well-known that the cyclohexane group is helpful for $\pi\cdots\pi$ stacking,[15] which makes the solubility of **OHHAH** (**3**) very poor. In addition, DMF is a poor solvent to cause aggregation of **OHHAH** (**3**).

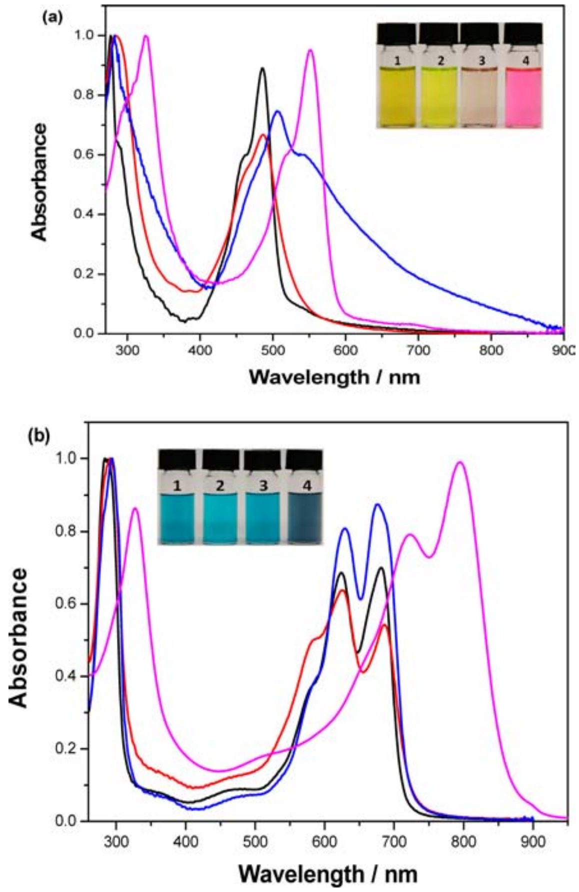


Figure 2. (a) Normalized absorption spectra of four compounds **1−4** in DMF solutions, concentration, 5 × 10^{-5} M. (b) Normalized absorption spectra of four compounds in TFA solutions, concentration, 5 × 10^{-5} M. Black line, **1**; red line, **2**; blue line, **3**; pink line, **4**. The insert shows the color changes in DMF (a) and TFA (b).

As shown in Figure 2a, the maximum absorptions of hexazapentacene derivatives **1−4** (5 × 10^{-5} M in DMF) are 485, 486, 507, and 551 nm (see Table 1), respectively. The corresponding calculated optical bandgaps for **TMHAP** (**1**), **TEHAP** (**2**), **OHHAH** (**3**), and **TTHAP** (**4**) are 2.55, 2.55, 2.45, and 2.25 eV. As observed in the previous report,[16] trifluoroacetic acid (TFA) could dramatically shift the UV−vis absorption of four hexazapentacene derivatives **1−4** to 670, 680, 670, and 810 nm, respectively, due to the protonation of N atoms in haxazapentacene backbones.

The electrochemical properties of hexazapentacene derivatives **1−4** in THF were studied in a three-electrode electrochemical cell with tetrabutyl-ammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) as electrolyte and Ag/AgCl as reference electrode (Figure 3 and Table 1). All materials exhibit one reversible reduction wave, suggesting that they have excellent electrochemical stability. No oxidation peaks (except for **4**, Supporting Information) were observed, indicating that they are intrinsic n-type organic semiconductors. The half-wave reduction potentials for **TMHAP** (**1**), **TEHAP** (**2**), **OHHAH** (**3**), and **TTHAP** (**4**) are −0.83, −0.87, −0.82, and −0.81 V, respectively, which correspond to the lowest unoccupied molecular orbital (LUMO) energy levels of −3.57, −3.53, −3.58, and −3.59 eV, using the empirical equation $E_{\mathrm{LUMO}} = -[4.4 + E^{\mathrm{red}}]$ eV.[17] Thiophene groups in **TTHAP** (**4**) have a big effect on the positions of HOMO and LUMO energy levels

Table 1. Physical Properties of Four Hexazapentacene Derivatives 1−4

Compounds	$E^{red}_{1/2}$ (V)[a]	LUMO (eV)[b]	HOMO (eV)[c]	E_{gap}/λ_{max}[(eV)[d]/nm]	LUMO (eV)[e]	HOMO (eV)[e]	E_{gap} (eV)[e]
1	−0.83	−3.57	−6.12	2.55/485	−3.21	−5.63	2.41
2	−0.87	−3.53	−6.08	2.55/486	−3.18	−5.60	2.41
3	−0.82	−3.58	−6.03	2.45/507	−3.21	−5.56	2.34
4	−0.81	−3.59	−6.14	2.25/551	−3.33	−5.48	2.15

[a] Obtained from cyclic voltammograms in tetrahydrofuran. Reference electrode: Ag/AgCl. [b] Calculated from cyclic voltammograms. [c] Calculated according to the formula $E_{HOMO} = E_{LUMO} - E_{gap}$. [d] Optical band gap, $E_{gap} = 1240/\lambda_{max}$. [e] Obtained from theoretical calculations.

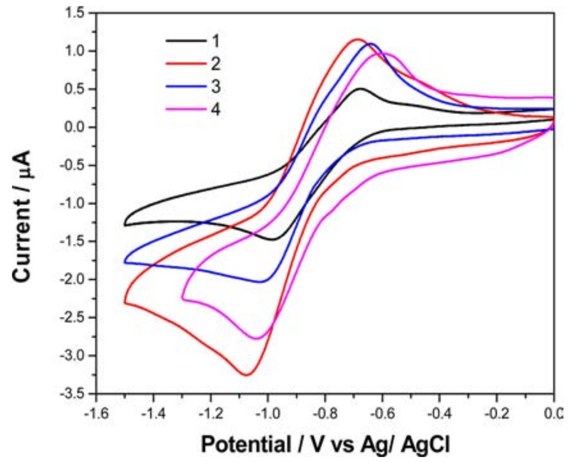


Figure 3. Cyclic Voltammetry curves of **1**−**4** in THF solution containing 0.1 M Bu_4NPF_6 electrolyte. Scanning rate: 50 mV/s.

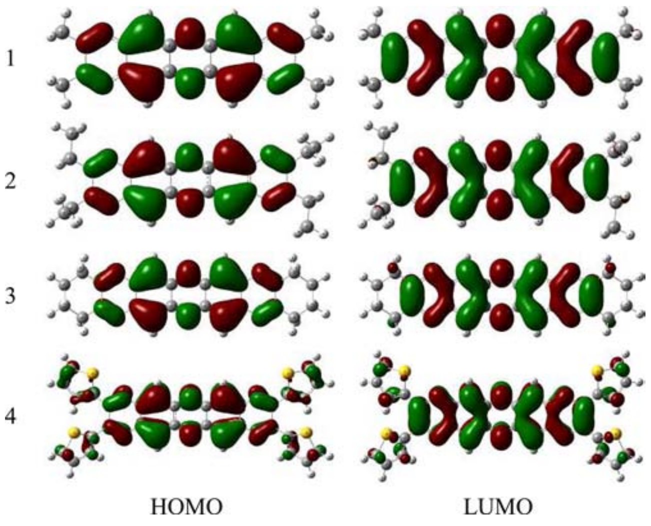


Figure 4. Wave functions for the HOMO and LUMO of hexazapentacene derivatives **1**−**4**.

compared to alkane substituted groups in **TMHAP** (**1**), **TEHAP** (**2**), and **OHHAH** (**3**).

The highest occupied molecular orbital (HOMO) energy levels of compounds **1**−**4** were calculated from the optical bandgap and LUMO levels, shown in Table 1. Clearly, the bandgaps of four new compounds were relatively larger than pentacene (1.77 eV) and hexacene (1.57 eV).[3a,h,18] It was found that the HOMO levels of as-synthesized four hexazapentacenes were lower than pentacene (−5.14 eV) and hexacene (−4.96 eV),[3a] indicating that they could show better stability in electronic devices. Moreover, LUMO levels of the four compounds were relatively lower than pentacene (−3.37 eV) but nearly identical with hexacene (−3.56 eV).[3a,18]

Electronic structures of novel compounds hexazapentacene derivatives **1**−**4** are theoretically investigated through calculation. The molecular geometries of **1**−**4** were optimized using density functional theory (DFT) at the B3LYP/6-31G* level.[19] The ground state frontier molecular orbitals of the optimized molecules were also calculated at the same level, as shown in Figure 4.

The HOMO and LUMO orbitals of compounds **1**−**3** are all delocalized on the hexazapentacene backbones. Not only are the HOMO and LUMO orbitals of **TTHAP** (**4**) delocalized on the hexazapentacene framework, but the thiophene groups also participated in the orbitals. The calculated band positions for all four compounds are presented in Table 1, which indicates that the calculated HOMO, LUMO energies and the bandgaps are close to the experimental results.

In conclusion, four novel hexazapentacene derivatives **1**−**4** have been successfully synthesized in efficient two steps from commercially available compounds. All materials have been investigated by photophysical and electrochemical methods. The reduction waves suggest that all materials are n-type semiconductors, which have potential applications in organic electronics. To the best of our knowledge, this is the first case where six N atoms are introduced into the pentacene backbone to form the conjugated molecules. Our method could offer a promising strategy to approach larger heteroacenes with more N atoms.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and supporting figures including, ^{13}CNMR for **TTHAP** (**4**), FT-IR, TGA, and high-solution mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

qczhang@ntu.edu.sg

Author Contributions

‡These authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Q.Z. acknowledges the financial support from AcRF Tier 1 (RG 18/09) and Tier 2 (MOE2012-T2-1-019, ARC 20/12) from MOE, CREATE program (Nanomaterials for Energy and Water Management) from NRF, and New Initiative Fund from NTU, Singapore. Y.Z. thanks the support from National Research Foundation of Singapore (Grant No. NRF-CRP-6-2010-2) National Research Foundation of Singapore (Grant Nos. NRF-CRP-5-2009-4 and NRF-CRP-6-2010-2).

■ REFERENCES

(1) (a) Zade, S. S.; Bendikov, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 4012. (b) Anthony, J. E. *Angew Chem., Int. Ed.* **2008**, *47*, 452. (c) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028. (d) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891.

(2) (a) Jiang, D.; Dai, S. *J. Phys. Chem. A* **2008**, *112*, 332K. (b) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K. N.; Carter, E. A.; Wudl, F. *J. Am. Chem. Soc.* **2004**, *126*, 7416. (c) Houk, N.; Lee, P. S.; Nenel, M. *J. Org. Chem.* **2001**, *66*, 5517.

(3) (a) Watanable, M.; Chang, Y. J.; Liu, S.-W.; Chao, T.-H.; Goto, K.; Yuan, Md. M. I. C.-H.; Tao, Y.-T.; Shinmyozu, T.; Chow, T. J. *Nat. Chem.* **2012**, *4*, 574. (b) Xiao, J.; Duong, H. M.; Liu, Y.; Shi, W.; Ji, L.; Li, G.; Li, S.; Liu, X.; Ma, J.; Wudl, F.; Zhang, Q. *Angew Chem,. Int. Ed.* **2012**, *51*, 6094. (c) Purushothaman, B.; Bruzek, M.; Parkin, S. R.; Miller, A.-F.; Anthony, J. E. *Angew Chem., Int. Ed.* **2011**, *50*, 7013. (d) Qu, H.; Chi, C. *Org. Lett.* **2010**, *12*, 3360. (e) Kaur, I.; Jazdzky, M.; Stein, N. N.; Prusevich, P.; Miller, G. P. *J. Am. Chem. Soc.* **2010**, *132*, 1261. (f) Kaur, I.; Stein, N. N.; Kopreski, R. P.; Miller, G. P. *J. Am. Chem. Soc.* **2009**, *131*, 342. (g) Chun, D.; Cheng, Y.; Wudl, F. *Angew Chem., Int. Ed.* **2008**, *47*, 8380. (h) Payne, M. M.; Parkin, S. R.; Anthony, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 8028. (i) Duong, H. M.; Bendikov, M.; Steiger, D.; Zhang, Q.; Sonmez, G.; Yamada, J.; Wudl, F. *Org. Lett.* **2003**, *5*, 4433.

(4) (a) Briseno, A. L.; Mannsfeld, S. C. B.; Ling, M. M.; Liu, S.; Tseng, R. J.; Reese, C.; Roberts, M. E.; Yang, Y.; Wudl, F.; Bao, Z. *Nature* **2006**, *444*, 913. (b) Aleshin, A. N.; Lee, J. Y.; Chu, S. W.; Kim, J. S.; Park, Y. W. *Appl. Phys. Lett.* **2004**, *84*, 5383. (c) De Boer, R. W.; Klapwijk, T. M.; Morpurgo, A. F. *Appl. Phys. Lett.* **2003**, *83*, 4345.

(5) (a) Xiao, J.; Liu, S.; Liu, Y.; Ji, L.; Liu, X.; Zhang, H.; Sun, X.; Zhang, Q. *Chem. Asian J.* **2012**, *7*, 561. (b) Zhang, Q.; Divayana, Y.; Xiao, J.; Wang, Z.; Tiekink, E. R. T.; Duong, H. M.; Zhang, H.; Boey, F.; Sun, X. W.; Wudl, F. *Chem.—Eur. J.* **2010**, *16*, 7422. (c) Xiao, J.; Divayana, Y.; Zhang, Q.; Duong, H. M.; Zhang, H.; Boey, F.; Sun, X. W.; Wudl, F. *J. Mater. Chem.* **2010**, *20*, 8167.

(6) Gorodetsky, A. A.; Cox, M.; Tremblay, N. J.; Kymissis, I.; Nuckolls, C. *Chem. Mater.* **2009**, *21*, 4090.

(7) (a) Miao, Q. *Synlett* **2012**, *23*, 326. (b) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876.

(8) Winkler, M.; Houk, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 1805.

(9) (a) Lindner, B. D.; Engelhart, J. U.; Märken, M.; Tverskoy, O.; Appleton, A. L.; Rominger, F.; Hardcastle, K. I.; Enders, M.; Bunz, U. H. F. *Chem.—Eur. J.* **2012**, *18*, 4627. (b) Lindner, B. D.; Engelhart, J. U.; Tverskoy, O.; Appleton, A. L.; Rominger, F.; Peters, A.; Himmel, H.-J.; Bunz, U. H. F. *Angew Chem., Int. Ed.* **2011**, *50*, 8588. (c) Appleton, A. L.; Brombosz, S. M.; Barlow, S.; Sears, J. S.; Bredas, J.-L.; Marder, S. R.; Bunz, U. H. F. *Nat. Commun.* **2010**, *1*, 91.

(10) Liang, Z.; Tang, Q.; Mao, R.; Liu, d.; Xu, J.; Miao, Q. *Adv. Mater.* **2011**, *23*, 5514.

(11) (a) He, Z.; Mao, R.; Liu, D.; Miao, Q. *Org. Lett.* **2012**, *14*, 4190. (b) He, Z.; Liu, D.; Mao, R.; Tang, Q.; Miao, Q. *Org. Lett.* **2012**, *14*, 1050. (c) Z. Liang, Z.; Tang, Q.; Xu, J.; Miao, Q. *Adv. Mater.* **2011**, *23*, 1535. (d) Liu, Y.-Y.; Song, C.-L.; Zeng, W.-J.; Zhou, K.-G.; Shi, Z.-F.; Ma, C.-B.; Yang, F.; Zhang, H.-L.; Gong, X. *J. Am. Chem. Soc.* **2010**, *132*, 16439. (e) Miao, Q.; Nguyen, T.-Q.; Someya, T.; Blanchet, G. B.; Nuckolls, C. *J. Am. Chem. Soc.* **2003**, *125*, 10284.

(12) (a) Wu, Y.; Yin, Z.; Xiao, J.; Liu, Y.; Wei, F.; Tan, K. J.; Kloc, C.; Huang, L.; Yan, Q.; Hu, F.; Zhang, H.; Zhang, Q. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1883. (b) Nishida, J. I.; Naraso, Murai, S.; Fujiwara, E.; Tada, H.; Tomura, M.; Yamashita, Y. *Org. Lett.* **2004**, *6*, 2007.

(13) Bunz, U. H. F. *Pure Appl. Chem.* **2010**, *82*, 953.

(14) Gajiwala, H. M.; Zand, R. *Polymer* **1999**, *41*, 2009.

(15) Locklin, J.; Li, D.; Mannsfeld, S. C. B.; Borkent, E. −j.; Meng, H.; Advincula, R.; Bao, Z. *Chem. Mater.* **2005**, *17*, 3366.

(16) Zucchero, A. J.; McGrier, P. L.; Bunz., U. H. F. *Acc. Chem. Res.* **2010**, *43*, 397.

(17) Hong, W.; Yuan, H.; Li, H.; Yang, X.; Gao, X.; Zhu, D. *Org. Lett.* **2011**, *13*, 1410.

(18) Tang, M. L.; Okamoto, T.; Bao, Z. *J. Am. Chem. Soc.* **2006**, *128*, 16002.

(19) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785.