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Syntheses and Crystal Structures of Benzohexathia[7]helicene and Naphthalene Cored Double Helicene

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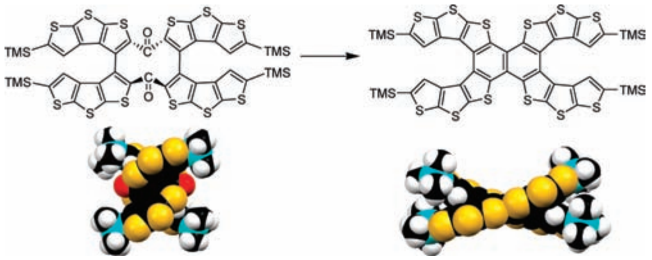
ABSTRACT



Bis(trimethylsilyl)benzohexathia[7]helicene 1, naphthalene cored double helicene 2 (the fused dimer of 1), and a novel ten-membered cyclic diketone with four moieties of dithieno[2,3-*b*:3′,2′-*d*]thiophene (3) were efficiently synthesized. Their crystal structures were determined with single-crystal X-ray analysis. In their crystal packings, they all show mutiple short contacts including intermolecular $\pi\cdots\pi$, $\pi\cdots$S, and S$\cdots$S interactions. UV/vis spectra indicate that significant π-electron delocalization existed in 1, 2, and 3.

The synthesis and characterization of thiophene-fused π-conjugated molecules and polymers are of current interest owing to their potential applications in organic optoelectronic materials and devices.[1−4] The heterohelicenes with thiophene units show attractive molecular structures with aesthetics. Recently, the improvements on synthesis of such heterohelicenes have been reported including new methods and their asymmetric syntheses.[5−7] Among the reported work, Rajca has published a series of synthetic work in carbon−sulfur helicenes[7] and studied their physical properties.[7c,8] In our recent work, we have also improved the synthetic method of making heptathia[7]helicene.[5a]

Herein, we describe the efficient syntheses and crystal structures of two novel heterohelicenes: benzohexathia[7]helicene, 5,5′-di(trimethylsilanyl)benzo[1,2-*b*:3,4-*b*′]bis(dithieno[2,3-*b*:3′,2′-*d*]thiophene) (*rac*-**1**), and highly π-extended naphthalene cored double helicence, 5,5′,5″,5‴-tetra(trimethylsilanyl)naphtho[1,2-*b*:3,4-*b*′:5,6-*b*″:7,8-*b*‴] tetra(dithieno[2,3-*b*:3′,2′-*d*]thiophene) (*rac*-**2**). In **2**, two helicenes of **1** fused together to form a naphthalene cored double helicene. The synthetic route to **1** and **2** is shown in Scheme 1. The starting material is 5,5′-di(trimethylsilanyl)-3,3′-bisdithieno[2,3-*b*:3′,2′-*d*]thiophene (**4**). The efficient synthesis of **4** (ca. 28% total yield with 3-bromothiophene as starting material) was reported in our previous work.[5a]

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(1) Murphy, A. R.; Fréchet, J.-M. J. *Chem. Rev.* **2007**, *107*, 1066–1096.

(2) Dadvand, A.; Cicoira, F.; Chernichenko, K. Y.; Balenkova, E. S.; Osuna, R. M.; Rosei, F.; Nenajdenko, V. G.; Perepichka, D. F. *Chem. Commun.* **2008**, 5354–5356.

(3) (a) Gao, P.; Beckmann, D.; Tsao, H. N.; Feng, X. L.; Enkelmann, V.; Baumgarten, M.; Pisula, W.; Müllen, K. *Adv. Mater.* **2009**, *21*, 213–216. (b) Tsao, H. N.; Cho, D.; Andreasen, J. W.; Rouhanipour, A.; Breiby, D. W.; Pisula, W.; Müllen, K. *Adv. Mater.* **2009**, *21*, 209–212.

(4) Liu, W. J.; Zhou, Y.; Ma, Y.; Cao, Y.; Wang, J.; Pei, J. *Org. Lett.* **2007**, *9*, 4187–4190.

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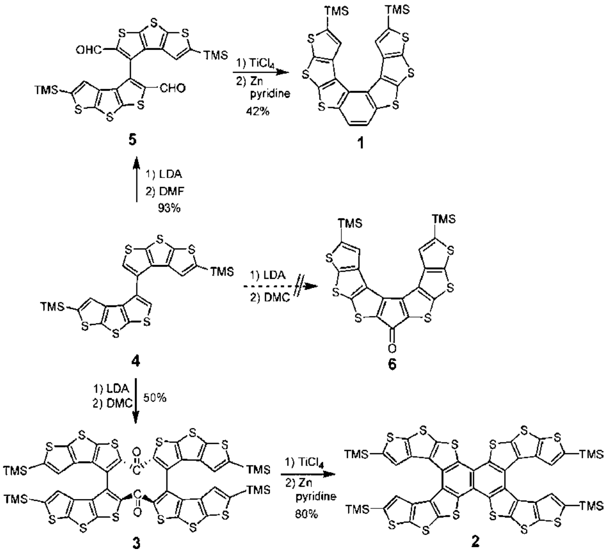
Scheme 1. Synthetic Route to **1** and **2**



Treatment of **4** with LDA generates the α-dilithiated compound. Quenching of this species with DMF affords 5,5′-di(trimethylsilanyl)-3,3′-bisdithieno[2,3-*b*:3′,2′-*d*]thiophene-2,2′-dialdehyde (**5**) in 93% yield. The intramolecular McMurry reaction[9] of **5**, using $TiCl_4$/Zn/pyridine, gives *rac*-**1** in 42% yield.

Alternatively, the essential innovation in our approach involved treatment of dilithiated **4** with *N*,*N*-dimethylcarbamyl chloride (DMC)[10] to afford an unexpected novel ten-membered cyclic diketone, a dimer of bis(5-trimethylsilanyl-dithieno[2,3-*b*:3′,2′-*d*]thiophen-2-yl)-methanone (**3**), bearing four arms of dithieno[2,3-*b*:3′,2′-*d*]thiophene (DTT), instead of the rigid helical ketone, **6**. Compared with the flexible ten-membered cyclic compound, **3**, the higher energy barrier should be overcome in making **6**, which is why none of **6** was observed in making **3**. The synthetic yield in making **3** is 50%. The intramolecular McMurry reaction of **3** was employed to generate the naphthalene cored double helicene, *rac*-**2**, in 80% yield under condition of $TiCl_4$−pyridine in dry THF. None of the side products such as oligomer or polymer from intermolecular McMurry reaction were observed. **2** is an amazing compound bearing four twist DTT arms to form double helical structure. The total yield of making **2** is ca. 40% with **4** as starting material and ca. 11% with 3-bromothiophene as starting material.

The structures of **1**, **2**, **3**, and **5** are all confirmed by single-crystal X-ray analysis. **5** belongs to the monoclinic space group *C*2/*c*. In **5**, the two moieties of DTT are nonplanar (Figure 1); C11−C10−C15−C14 torsion is 52.7°; and C12−C11−C14−C13 torsion is 75.7°; however, each moiety of DTT is approximately coplanar, and the torsions are 0.9° (C5−C6−C8−C10) and 6.5° (C15−C16−C18−C20), respectively. The dihedral angle between the two moieties of DTT is 55.6°. The distance between H5···H20 is 3.175 Å.

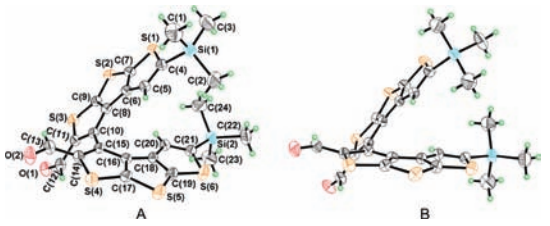


Figure 1. Molcular structure and conformation for **5**. Top view: (A). Side view: (B). Carbon, oxygen, silicon, and sulfur atoms are depicted with thermal ellipsoids set at the 30% probability level.

With the formation of the middle benzene ring from **5** to **1**, the molecule of **1** is compressed into a helical structure (Figure 2A and Figure 2B). By slow evaporation of solution of **1** in a mixture solvent of $CHCl_3$ and CH_3OH (1:3, v/v), two kinds of crystals of **1** were obtained at the same time. One had a slight pink color and belongs to the orthorhombic system, space group *Pbca* (Figure 2C), and another one is colorless in the triclinic system, space group P-1 (Figure 2D). The structural parameters of **1** in an orthorhombic crystal and triclinic crystal are nearly similar. For example, two distances between H2···H17 are 2.725 and 2.711 Å; two interplanar angles between the terminal thiophene rings are 46.7° and 52.1°; two inner (C17, C16, C13, C12, C7, C6, C3, C2) helixes climb 2.611 and 2.695 Å and turn in-plane by 293.6° and 295.6°, respectively.

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(5) New reports about the synthesis of helicenes: (a) Li, C.; Shi, J.; Xu, L.; Wang, Y.; Cheng, Y.; Wang, H. *J. Org. Chem.* **2009**, *74*, 408–411. (b) Adriaenssens, L.; Severa, L.; Šálová, T.; Císařová, I.; Pohl, R.; Šaman, D.; Rocha, S. V.; Finney, N. S.; Pospíšil, L.; Slavíček, P.; Teplý, F. *Chem.—Eur. J.* **2009**, *15*, 1072–1076. (c) Sehnal, P.; Stará, I. G.; Šaman, D.; Tichý, M.; Míšek, J.; Cvačka, J.; Rulíšek, L.; Chocholoušová, J.; Vacek, J.; Goryl, G.; Szymonski, M.; Císařová, I.; Starý, I. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 13169–13174. (d) Latorre, A.; Urbano, A.; Carreño, M. C. *Chem. Commun.* **2009**, 6652–6654. (e) Tanaka, K.; Fukawa, N.; Suda, T.; Noguchi, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 5470–5473. (f) Pieters, G.; Gaucher, A.; Prim, D.; Marrot, J. *Chem. Commun.* **2009**, 4827–4828. (g) Graule, S.; Rudolph, M.; Vanthuyne, N.; Autschbach, J.; Roussel, C.; Crassous, J.; Réau, R. *J. Am. Chem. Soc.* **2009**, *131*, 3183–3185. (h) Míšek, J.; Teplý, F.; Stará, I. G.; Tichý, M.; Šaman, D.; Cisaová, I.; Vojtíšek, P.; Starý, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 3188–3191. (i) Ichikawa, J.; Yokota, M.; Kudo, T.; Umezaki, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 4870–4873. (j) Sehnal, P.; Krausová, Z.; Teplý, F.; Stará, I. G.; Starý, I.; Rulisek, L.; Šaman, D.; Cisaová, I. *J. Org. Chem.* **2008**, *73*, 2074–2082. (k) Carreño, M. C.; Enríquez, Á.; García-Cerrada, S.; Sanz-Cuesta, M. J.; Urbano, A.; Maseras, F.; Nonell-Canals, A. *Chem.—Eur. J.* **2008**, *14*, 603–620. (l) Grandbois, A.; Collins, S. K. *Chem.—Eur. J.* **2008**, *14*, 9323–9329.

(6) For recent reviews on synthesis of helicenes, see: (a) Rajca, A.; Miyasaka, M. *Synthesis and Characterization of Novel Chiral Conjugated Materials, Functional Organic Materials: Syntheses and Strategies*; Müeller, T. J. J., Bunz, U. H. F., Eds.; Wiley-VCH: Weinheim, Germany, 2007; pp 543−577. (b) Rajca, A.; Rajca, S.; Pink, M.; Miyasaka, M. *Synlett* **2007**, 1799–1822. (c) Collins, S. K.; Vachon, M. P. *Org. Biomol. Chem.* **2006**, *4*, 2518–2524. (d) Torroba, T.; García-Valverde, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 8092–8096. (e) Urbano, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3986–3989.

(7) Rajca's work on carbon-sulfur [*n*]helicenes: (a) Miyasaka, M.; Pink, M.; Rajca, S.; Rajca, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 5954–5957. (b) Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2005**, *127*, 13806–13807. (c) Rajca, A.; Miyasaka, M.; Pink, M.; Wang, H.; Rajca, S. *J. Am. Chem. Soc.* **2004**, *126*, 15211–15222. (d) Miyasaka, M.; Pink, M.; Rajca, A.; Rajca, S. *Chem.—Eur. J.* **2004**, *10*, 6531–6539. (e) Miyasaka, M.; Rajca, A. *Synlett* **2004**, 177–181. (f) Rajca, A.; Wang, H.; Pink, M.; Rajca, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4481–4483.

(8) (a) Rajca, A.; Miyasaka, M.; Pink, M.; Xiao, S.; Rajca, S.; Das, K.; Plessel, K. *J. Org. Chem.* **2009**, *74*, 7504–7513. (b) Friedman, T. B.; Cao, X.; Rajca, A.; Wang, H.; Nafie, L. A. *J. Phys. Chem. A* **2003**, *107*, 7692–7696.

(9) (a) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513–1524. (b) Dai, W.; Mak, W. L. *Tetrahedron Lett.* **2000**, *41*, 10277–10280.

(10) Lucas, P.; Mehdi, N. E.; Ho, H. A.; Bélanger, D.; Breau, L. *Synthesis* **2000**, *9*, 1253–1258.

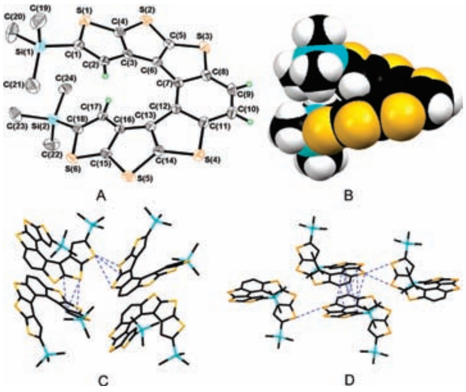

Figure 2. Molcular structure and conformation for **1**. Top view: (A). Carbon, oxygen, silicon, and sulfur atoms are depicted with thermal ellipsoids set at the 30% probability level. The hydrogen atoms from TMS groups are omitted for clarity. Side view in spacefill mode (B). Crystal packings of *rac*-**1** in orthorhombic, *Pbca* space group (C), and triclinic, P-1 space group (D).

However, the crystal packings of **1** in the two kinds of crystals are different. In orthorhombic crystal (*Pbca* space group), the molecules of (*R*)-**1** and (*S*)-**1** are packing one by one along both the *a*-axis and the *b*-axis (Figure 2C). In the triclinic crystal (P-1 space group), the molecules of (*R*)-**1** and (*S*)-**1** are packing in each row along the *b*-axis (Figure 2D). The $\pi\cdots\pi$, $\pi\cdots$S, and S···S interactions are clearly observed in both crystals. For example, S3···S5, 3.647 Å; S3···S6, 3.373 Å; S3···C11, 3.887 Å; C2···C9, 3.488 Å; and C3···C10, 3.325 Å are observed in the triclinic crystal.

3 is a novel ten-membered macrocyclic diketone with four DTT arms, and a chiral π-conjugated molecule possessed approximately a D_2 point group of symmetry (Figure 3A). *Rac*-**3** crystallizes in triclinic, space group P-1. In *rac*-**3**, the central cyclodecatetraene ring containing two carbonyl group has a twist "saddle" form. The dihedral angles between two opposite DTTs to form the "saddle" are 40.2° and 61.2° for (*S*,*S*)-**3** and 37.2° and 61.3° for (*R*,*R*)-**3**. Each of the four DTTs in (*R*,*R*)-**3** or (*S*,*S*)-**3** is approximately coplanar. The biaryls in molecule **3** adopt transoid conformations, and each biaryl has a chiral axis with the same configurations. Therefore, **3** shows somewhat of a double-helical conformation, in which two moieties of bis(5-trimethylsilanyl-dithieno[2,3-*b*;3′,2′-*d*]thiophen-2-yl)-methanone embraced together pointing away from each other (Figure 3B).

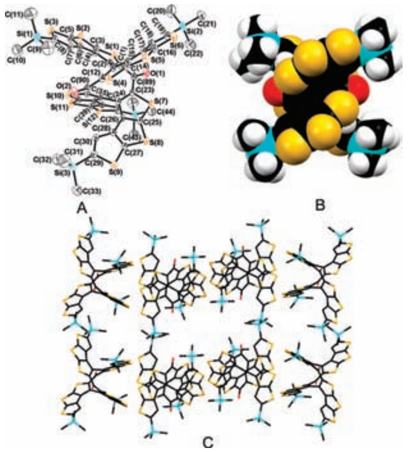

Figure 3. Molecular structure and conformation for **3**. Side view (A). Carbon, oxygen, silicon, and sulfur atoms are depicted with thermal ellipsoids set at the 30% probability level. All hydrogen atoms are omitted for clearity. Side view in spacefill mode (B). The crystal packing of *rac*-**3** (C). All hydrogen atoms from *rac*-**3** and chloroform molecules in the crystal are omitted for clarity.

In packing of **3**, eight molecules per unit cell are shown along the *b*-axis (Figure 3C). Each molecule combines with one molecule of chloroform. The packing shows columns of independent molecules, and these columns array alternately with (*R*,*R*)-**3**···(*R*,*R*)-**3**···(*S*,*S*)-**3**···(*S*,*S*)-**3** along the *c*-axis. Each (*R*,*R*)-**3**···(*R*,*R*)-**3** or (*S*,*S*)-**3**···(*S*,*S*)-**3** shows the array of perpendicularity. Multiple S···S and $\pi\cdots$S interactions are found between (*R*,*R*)-**3** and (*S*,*S*)-**3**. For example, the distances of S5···S7, 3.599 Å; S6···S7, 3.573 Å; S6···S8, 3.787 Å; S6···C25, 3.450 Å; S6···S5, 3.721 Å; and C16···C16, 3.751 Å are observed.

The molecular structure of **2** could be regarded as a dimer of **1** with an approximate C_2 point group of symmetry (Figure 4A). **2** shows a novel double helical conformation, in which two helical structures are fused together pointing away from each other (Figure 4B). **2** crystallizes in the orthorhombic, space group $P2_12_12_1$. In packing of *rac*-**2**, (*R*,*R*)-**2** and (*S*,*S*)-**2** are embraced orthogonally together to form a "couple" due to multiple short interactions including S···S and $\pi\cdots$S interac-

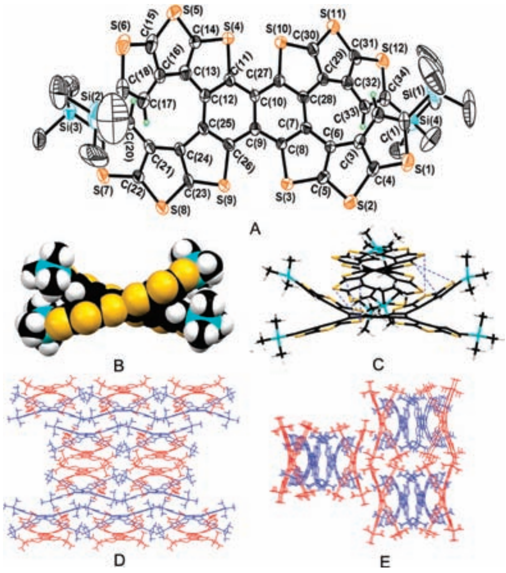

Figure 4. Molecular structure and conformation for **2**. Top view (A). Carbon, oxygen, silicon, and sulfur atoms are depicted with thermal ellipsoids set at the 30% probability level. All hydrogen atoms from the TMS group are omitted for clarity. Side view in spacefill mode (B). The S···π and S···S interactions between (*R*,*R*)-**2** and (*S*,*S*)-**2** in a "couple" (C). The crystal packing of *rac*-**2**: along *a*-axis (D) and *b*-axis (E).

tions in the "couple" (Figure 4C). For example, the distances of S11···S23, 3.743 Å; C2···S22, 3.460 Å; C23···S20, 3.453 Å; C30···S23, 3.501 Å; and C79···S4, 3.420 Å are observed, respectively. The repulsion of the facing terminal thiophene rings causes two interplanar angles between the terminal thiophene rings, 54.6° and 55.4° for (*R*,*R*)-**2** and 57.2° and 50.5° for (*S*,*S*)-**2**, respectively. The distances of H2A···H33A and H17A···H20A are 2.850 and 2.844 Å for (*R*,*R*)-**2**, and the distances of H48A···H79A and H63A···H66A with 2.779 and 2.873 Å are found for (*S*,*S*)-**2**. With the middle benzene rings as reference, the inner helixes of (C33, C32, C29, C28, C7, C6, C3, C2) and (C17, C16, C13, C12, C25, C24, C21, C20) in (*R*,*R*)-**2** climb 2.911 and 2.873 Å and turn in-plane by 306.6° and 305.1°, respectively. For the case of (*S*,*S*)-**2**, the inner helixes of (C63, C62, C59, C58, C71, C70, C67, C66) and (C48, C49, C52, C53, C74, C75, C78, C79) climb 2.929 and 2.851 Å and turn in-plane by 310.0° and 306.9°, respectively.

In *rac*-**2**, the packing shows rows of the couples "π-stacked" along the crystallographic *a*-axis and *b*-axis (Figure 4D and 4E). The enantiomers (in blue and red color, respectively) are neighboring between two rows of the couples. Multiple short interactions including S···S, π···S, and π···π interactions could also be observed among the rows. For example: S14···S16, 3.820 Å; S13···C58, 3.886 Å; S14···C60, 3.677 Å; C48···C63, 3.792 Å; and C50··· C59, 3.812 Å.

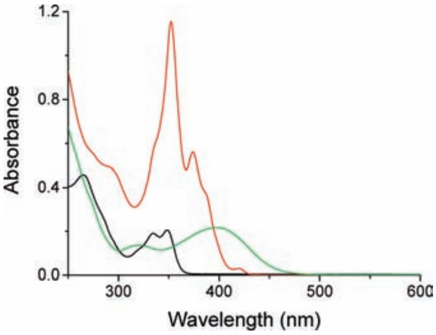

Figure 5. Absorption spectra for **1** (black), **2** (red), and **3** (green) in chloroform at room temperature ([C] = 1 × 10^{-5} M).

The UV/vis spectra for **1**, **2**, and **3** are shown in Figure 5. The integrated absorbance in **2** is approximately a treble increase compared to that of **1** and a double increase compared to that of **3**. **1** has π-electron delocalization including both helical distortion and possible conjugation through the sulfur atoms with two major absorption peaks at 332 and 347 nm. **3** has four approximately planar DTTs, and the average dihedral angle between two DTTs linked to the carbonyl group in **3** is ca. 47.9°, which means existing conjugation among two DTTs linked to the carbonyl group. In addition, the carbonyl group could be regarded as an auxochromic group, so **3** shows the low energy gap with a broad absorption peak at ca. 400 nm. **2** also has four approximately planar DTTs, which are fused and conjugated with a naphthalene core with two absorption peaks at 351 and 373 nm and a shoulder peak at 388 nm. Compared with the case of **1**, the bathochromic shift for **2** is rather substantial, due to its increased π-electron delocalization. However, without an auxochromic group, **2** reveals the blue shift compared with the case of **3**.

In summary, the synthetic approach to three novel helical compounds, **1**, **2**, and **3**, was efficiently developed. In crystal packings, **1**, **2**, and **3** show multiple short contacts including π···π, π···S, and S···S interactions. Such types of compounds might be used as novel materials in organic functional materials.[7c,11−15] More work in OFET and chirality for these compounds is in progress.

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Supporting Information Available: Synthesis and characterization of all compounds and crystallographic CIF files of **1**, **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) (a) Zhang, L.; Tan, L.; Wang, Z.; Hu, W.; Zhu, D. *Chem. Mater.* **2009**, *21*, 1993–1999. (b) Tan, L.; Zhang, L.; Jiang, X.; Yang, X.; Wang, L.; Wang, Z.; Li, L.; Hu, W.; Shuai, Z.; Li, L.; Zhu, D. *Adv. Funct. Mater.* **2009**, *19*, 272–276.

(12) Bromley, S. T.; Mas-Torrent, M.; Hadley, P.; Rovira, C. *J. Am. Chem. Soc.* **2004**, *126*, 6544–6545.

(13) Sundar, V. C.; Zaumseil, J.; Podzorov, V.; Menard, E.; Willett, R. L.; Someya, T.; Gershenson, M. E.; Rogers, J. A. *Science* **2004**, *303*, 1644–1646.

(14) Xue, J.; Forrest, S. R. *Appl. Phys. Lett.* **2001**, *79*, 3714–3716.

(15) Pappenfus, T. M.; Chesterfield, R. J.; Frisbie, C. D.; Mann, K. R.; Casado, J.; Raff, J. D.; Miller, L. L. *J. Am. Chem. Soc.* **2002**, *124*, 4184–4185.