JOC Article

Synthesis and Structure of Alkyl-Substituted Fused Thiophenes Containing up to Seven Rings

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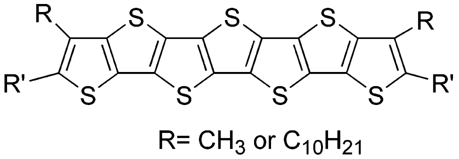

R= CH_3 or $C_{10}H_{21}$

R'=H or $C_{10}H_{21}$

We have established a series of synthetic methods to synthesize alkyl-substituted fused thiophenes with degrees of fusion from two to seven rings. These fused thiophene ring compounds have very good solubility in common organic solvents, making possible the solution processing of these compounds for electronic applications. The UV absorption of these fused thiophenes is blue-shifted when compared with their hydrocarbon counterparts. The larger band gaps result in much better stability. Single-crystal X-ray results for 3,6-didecanyldithieno[2,3-*d*:2′,3′-*d*′]thieno[3,2-*b*:4,5-*b*′′]dithiophene (**FT5**) and 3,7-didecanylthieno-[3,2-*b*]thieno[2′,3′:4,5]thieno[2,3-*d*]thiophene (**FT4**) demonstrate that both compounds form π-stacking structures instead of a herringbone-type of packing motif. This more favorable π-stacked structure may lead to better material electronic properties such as mobility in devices fabricated with these compounds.

Introduction

Conjugated organic molecules such as pentacene have been widely used as organic field-effect transistor (FET) materials. Mobilities exceeding 1 $cm^2/V{\cdot}s$ have been achieved.[1,2] It has been shown that good organic FET materials need to possess good π-stacking structures in the solid state.[3] One previous report indicated that pentacene (**I**) films exhibited essentially single-crystal-like macroscopic morphology.[3] Although the charge carrier mobility mechanism for organic FET materials is still not fully understood, a fully extended π system is essentially needed to achieve higher mobility in an all organic system. Extension of the π system in a single molecule should lead to increased π stacking, which could result in increased charge carrier mobility. However, in most cases, extension of conjugation also causes other problems. First, increased conjugation tends to lead to a decreased band gap, which makes the molecule degrade easier in oxygen environments. Second, extensively conjugated organic molecules usually have very limited solubility, thus limiting their processibility. A recent report from Anthony et al.[4] on the synthesis of acenedithiophenes with up to seven linearly fused ring units tends to support this trend. Acenedithiophenes have absorption maxima near 760 nm and can only be stored in oxygen-free toluene. Pentacene itself suffers the same instability and insolubility problems.[5] In contrast, fused thiophene compounds have exhibited very good environmental stability due to their larger band gaps, as stated in several recent publications.[6−8] Pentathienoacene (**III**) (Figure 1), for example, has a maximum

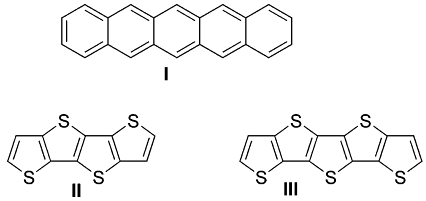

FIGURE 1. Pentacene, tetrathienoacene, and pentathienoacene.

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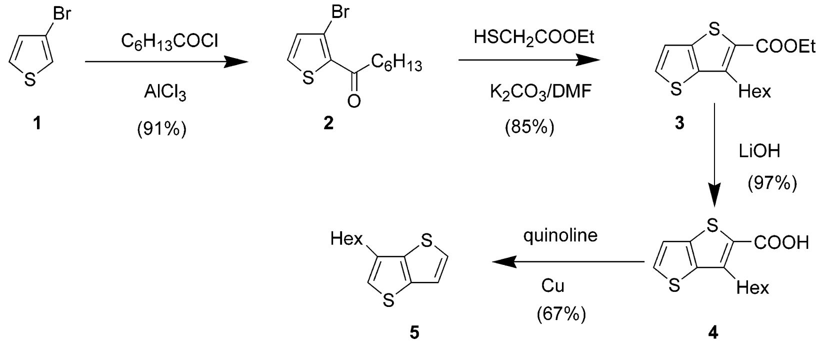
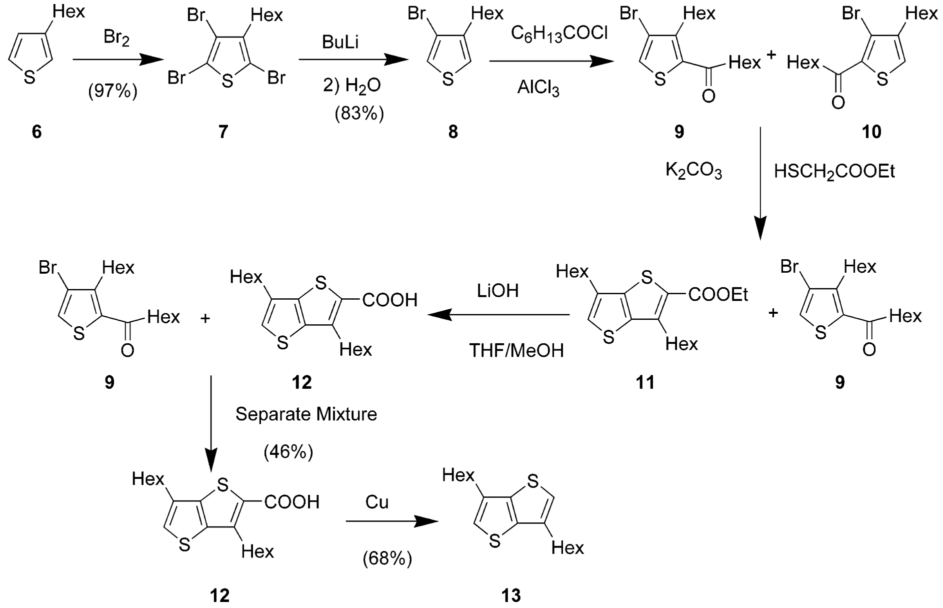
10.1021/jo061853y CCC: $37.00

SCHEME 1. Monosubstituted Thienothiophene



SCHEME 2 *β*-Disubstituted Alkylthienothiophenes



absorption at 357 nm,[6,9] and the newly synthesized heptathienoacene has an absorption maximum at 396 nm.[6] Compared with pentacene's 575 nm and acenedithiophene's 760 nm absorption maxima,[10] the fused thiophene compounds absorb at a much higher energy level. Although, previously, pentathienoacene was reported to gradually decompose to give a greenish solution in chloroform due to possible oxidation,[9] a device fabricated in a recent report indicated that pentathienoacene is quite stable.[7] Direct current (dc), electronic resistivity measurements of crystalline tetrathienoacene (**II**) at room temperature in dry air demonstrated a resistivity of $\rho = 1.7 \times 10^{12}$ Ω·cm that is in the same range as that of the nine benzene ring compound, violanthrene ($\rho = 3.7 \times 10^{12}$ Ω·cm).[11] These data indicate that tetrathienoacene has the potential to be a very good organic semiconductor. A recent report from Zhu[7] has confirmed that pentathienoacene is a semiconductor with a measured mobility of 0.045 cm^2/V·s and an on/off ratio of 10^3. This is the first time pentathienoacene was successfully tested as an organic semiconductor in a FET device.

The thiophene moiety, as in 3-alkylthiophene, has been successfully used in organic−electronic and optical applications due to its unique electronic and optical properties.[12−16] Oligomeric thiophenes have also been successfully employed as the active components in organic FET and light-emitting devices.[17−19] Recently, McCulloch et. al.[20] reported a new polymer system which contains a two-ring fused thiophene moiety. A mobility of 0.6 cm^2/V·s was reported. However, the majority of the

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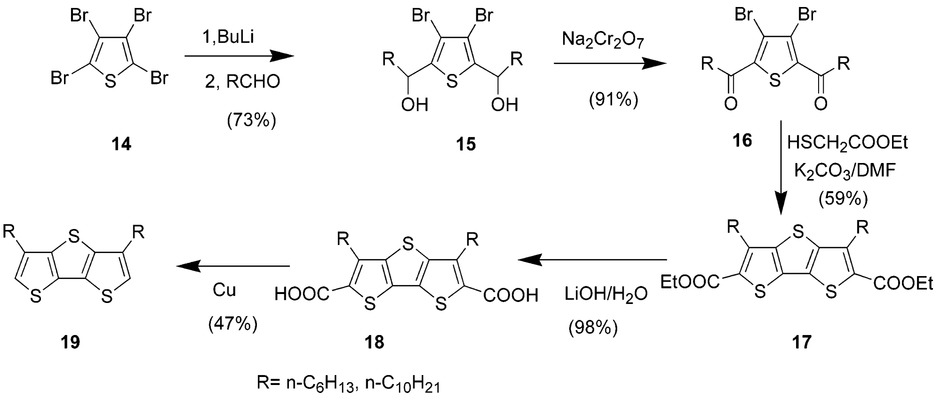
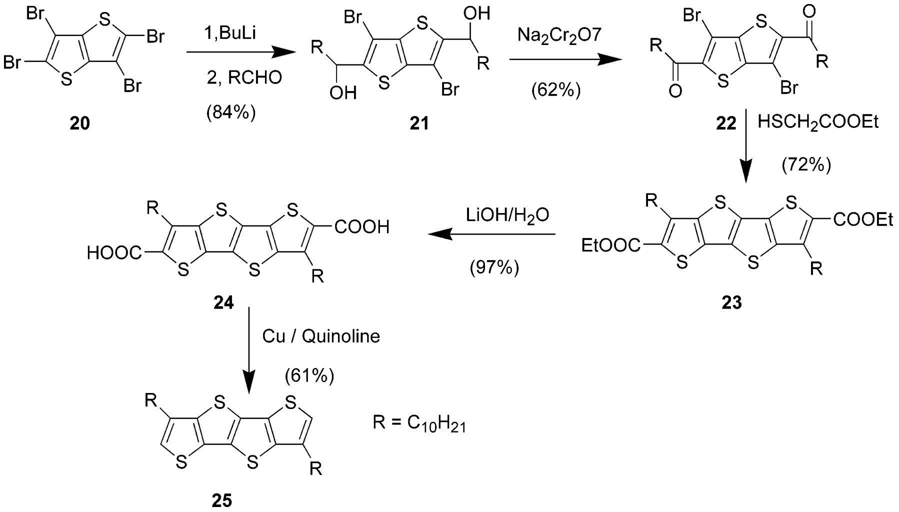
SCHEME 3. Synthesis of Three-Membered, Alkyl-Substituted Fused Thienothiophenes



SCHEME 4. Synthesis of Alkyl-Substituted, Four-Membered Fused Thienothiophenes



thiophene materials reported in organic−electronic device applications are still α-oligothiophenes. There are only a few examples using fused thiophene systems for semiconductor applications.[7,21,22] This is due to the following reasons: (1) fused thiophenes, such as pentathienoacene, have poor solubility and (2) synthetic methodologies, especially for the formation of fused thienothiophenes with more than four member rings, are limited.[6,7,9,23] More recently, Yamaguchi reported an efficient synthetic route by using a triple cyclization of bis(*o*-haloaryl)-diacetylenes to synthesize fused rings,[24] but this method is limited to odd-number fused ring synthesis.

During the past several years,[25] we have developed a series of synthetic methods to prepare several alkyl-substituted fused thiophenes with up to seven fused rings. The alkyl groups can be distributed in either α, *β*, or both the α and *β* positions of the fused ring. We believe that our synthetic methods supply a systematic tool for synthesis of different size fused thiophenes. By varying the size of fused thiophene compounds in FET devices, we should be able to obtain more fundamental knowledge of structure−property relationships. We also envision that, by engineering the length of the side chains, we can achieve good solid-state molecular packing along with high solubility and processibility. Ultimately, these materials can be utilized in solution-processing methods, such as ink jet printing, to achieve high quality organic semiconductor materials.

Results and Discussion

Synthesis of *β*-Alkyl-Substituted Thienothiophene Two Fused Ring Systems. An initial attempt to synthesize the alkyl-substituted fused thiophenes from 3,6-dibromothieno-[3,2-*b*]thiophene[26] was made using a coupling reaction of the appropriate Grignard reagent catalyzed with 1,3-bis-(diphenylphosphino)propanedichloronickel(II), which was used successfully for the synthesis of 3-alkylthiophene and 3,4-dialkylthiophenes.[27,28] It was found that this coupling reaction was not suitable for fused thiophene compounds. We are not sure of the reasons at this moment, but the rigidity change and electron distribution change may all have contributed to this result. Thus, an alternative approach where the alkyl groups

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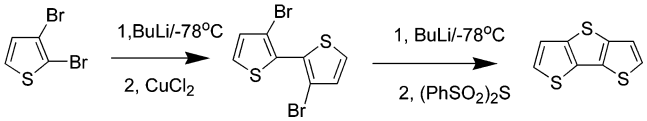
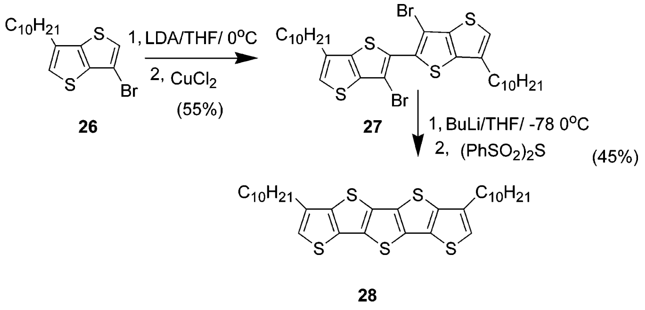
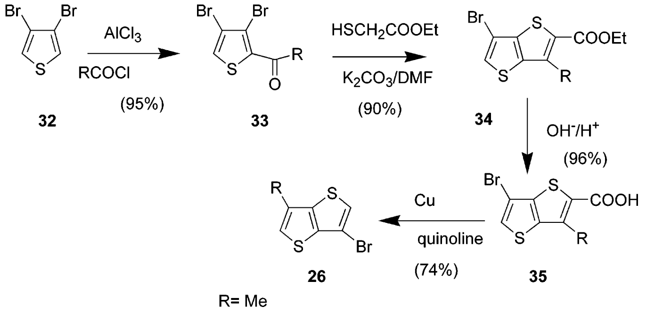
SCHEME 5. Hellberg's Improved Method



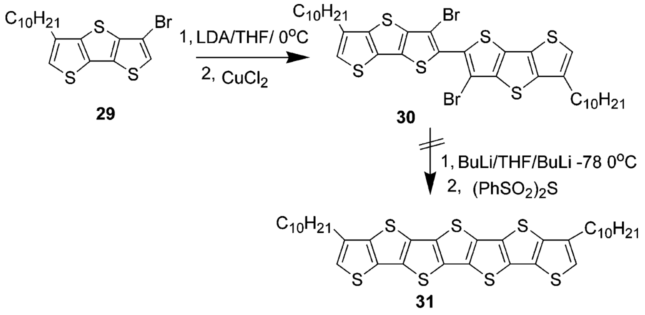
SCHEME 6. Synthesis of Five-Membered, *β*-Disubstituted Fused Thienothiophenes



SCHEME 7. Synthesis of 3-Bromo-6-alkylthieno[3,2-*b*]thiophene



SCHEME 8. Unsuccessful Synthesis of Seven-Membered, *β*-Disubstituted Fused Thienothiophenes



are added during the ring closure step was taken. The monosubstituted, two fused thiophene ring compound was synthesized from 3-bromothiophene using the methodology reported by Matzger et al.[29] (Scheme 1).

Although the di-β-substituted, two fused thiophene ring system was also reported by Matzger,[29] we decided to develop an alternative synthetic route by using a ketone-based ring closure procedure for the synthesis of di-β-substituted alkylthienothiophenes (Scheme 2). Although this route is less efficient, these reaction steps can be finished very quickly with no separations required until the desired acid compound **12** is formed. Compound **7**, resulting from the bromination of **6**, was partially debrominated by butyllithium to give **8**. A Friedel−Crafts reaction of **8** at 0 °C gave a mixture of **9** and **10** in an approximate 1:3 ratio based on GC/MS analysis. The separation of these isomers was not attempted. The mixture was used directly for the next step since the ring closure reaction can only take place on compound **10**, leaving compound **9** unreacted. After hydrolysis of the mixture, **12** could easily be separated from **9**. Decarboxylation of **12** yielded compound **13** as a waxy white solid.

Synthesis of Three- and Four-Membered *β*-Alkyl-Substituted Fused Thienothiophenes. Although dimethyl and diphenyl dithienothiophenes (three fused thiophene rings) have been previously synthesized,[30−32] there are no effective methodologies to make the long alkyl-chain derivatives in a convenient way. Likewise, alkyl-substituted, four fused thiophene ring compounds have not been reported in the literature so far. The previous three-ring syntheses included two, two-step reactions. First, butyllithium was used to generate an anion from 3-bromo-4-alkylthiophene, followed by the addition of SCl_2 or $(PhSO_3)_2S$ as a coupling reagent. Second, the connected bisthienylsulfide was treated again with butyllithium, followed by addition of $CuCl_2$ to oxidize the dianion for ring closure. Since the dianions are generated by butyllithium without any selectivity, this reaction results in only moderate yields. Alternatively, Holmes et al.[33] reported using 2,5-diformyl-3,4-dibromothiophene to synthesize the unsubstituted fused three-ring compound. Following our strategy for alkyl-substituted thienothiophenes, we used diketones for ring closure. An attempt to run a Friedel−Crafts diacylation reaction on 3,4-dibromothiophene produced only a monoketone on the thiophene ring. Apparently, the first aliphatic carbonyl deactivates the ring toward further acylation. Since cation chemistry proved unfruitful, anion chemistry was employed. Starting with 2,3,4,5-tetrabromothiophene (**14**) and butyllithium, the 2,5-dilithio-3,4-dibromothiophene dianion was generated at −78 °C (Scheme 3). The dianion was quenched with the appropriate aldehyde to yield the desired dialcohols. The dialcohol was easily oxidized to the corresponding diketone using Jones' reagent. The β-dialkyl-substituted fused thienothiophenes were obtained in reasonably good yields following the ring closure procedure used for the two-ring system.

Fused thiophenes comprised of four fused rings were also synthesized using the same method, as illustrated in Scheme 4. The desired starting compound, 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene, **20**, was obtained according to Fuller and Smith's report.[26] This compound was mixed with dry THF before being reacted with butyllithium at −78 °C. The resulting dianion was then quenched with the aldehyde. Although the starting material was not totally dissolved in the solvent, the dialcohol was obtained in a good yield.

Synthesis of Five- and Seven-Membered Alkyl-Substituted Fused Thienothiophenes. The design of a synthetic route to prepare alkyl-substituted, five-membered fused thiophene materials was more challenging. Hellberg's[34] improvements to Jong's and Janssen's previous synthesis of dithienothiophene[35]

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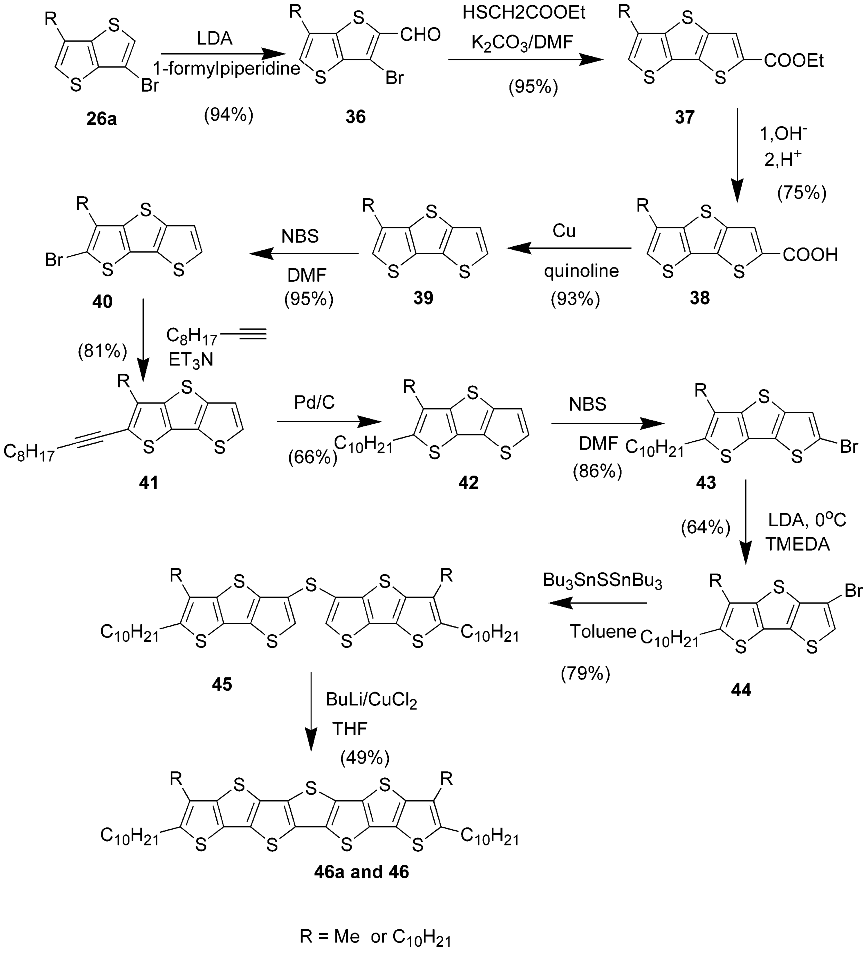
SCHEME 9. Synthesis of Tetra-Substituted Fused Thiophene



was considered. In the original work, 3-thienyllithium was generated from 3-bromothiophene at −78 °C, followed by reaction with bis(phenylsulfonyl)sulfide to form 3,3′-dithienyl sulfide. This sulfide was reacted again with butyllithium at low temperature (−78 °C) and oxidized by $CuCl_2$ to produce the desired three-membered fused thiophene. Usually, good yields are obtained for the first step due to the high reactivity of 3-thienyllithium with bis(phenylsulfonyl)sulfide. However, the second step usually gives poor yields due to low selectivity during lithiation of the 3,3′-dithienyl sulfide. In order to improve the yield, Hellberg et al.[34] used 2,3-dibromothiophene as the starting material. In this case, both the oxidation reaction ($CuCl_2$) and the ring closure reaction using bis(phenylsulfonyl)sulfide gave good yields due to better selectivity in generating the appropriate anions during the lithiation (Scheme 5).

Hellberg's approach still has some limitations. First, the α,β-dibromothiophene is very difficult to obtain. Second, all of the reactions were run at −78 °C, which limits the synthesis of some larger fused thiophene ring systems due to solubility issues. To circumvent these issues, we considered the work of Fuller et al. again.[26] In their report, when lithium diisopropylamide (LDA) reacts with 3-bromothiophene at 0 °C, the deprotonation occurs almost exclusively in the α position. Although we did not find any reports using LDA/$CuCl_2$ for oxidative coupling reactions, we tested the feasibility using 3-bromothiophene as the starting material to react with LDA at 0 °C. The coupled compound could be successfully obtained by reaction of the anion with $CuCl_2$. On the basis of this very promising result, we designed a method to synthesize five-membered fused thiophenes, as shown in Scheme 6.

The key intermediate for this synthesis is compound **26**. The corresponding synthetic scheme for synthesis of **26** is very straightforward and is shown in Scheme 7. The 3,4-dibromothiophene, **32**, was treated under Friedel−Crafts acylation conditions and only gave a single acylated product, **33**. This ketone was reacted with ethyl thioglycolate to close the ring. Finally, compound **26** was obtained by decarboxylation of acid **35** in quinoline with a copper catalyst. However, when we tried the same set of reactions to form a seven-membered fused thiophene ring (Scheme 8), the ring closure reaction did not proceed well. Since compound **30** is a highly crystalline solid, it can only dissolve into hot toluene and other aromatic solvents. It is possible to dissolve compound **30** in hot THF, but the Hellberg[34] reaction is usually conducted at −78 °C, and at this low temperature, all of the material precipitated out from the solvent and no reaction was observed. Almost all of the starting material could be recovered after workup without loss of bromine after treating **30** with butyllithium at −78 °C. The reaction was also attempted at 0 °C in hexane, and similar results were obtained.

In order to synthesize seven-membered fused thiophene rings with appropriate solubility, two more alkyl substituents were added to the ring. This synthetic route is illustrated in Scheme 9. Two versions of compound **26** were prepared, **26** with R = n-$C_{10}H_{21}$ and **26a** with R = CH_3. Treatment of **26a** with LDA followed by 1-formylpiperidine at 0 °C resulted in incorporation

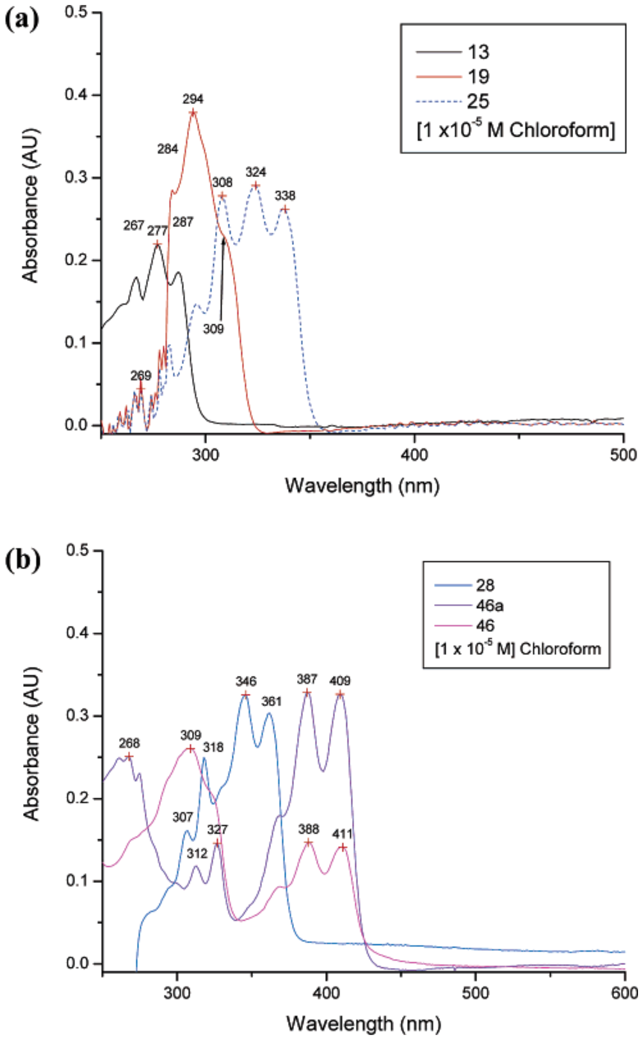


FIGURE 2. (a and b) UV−vis spectra of fused thienothiophenes. (a) FT2, FT3, and FT4 absorption spectra. (b) FT5 and two FT7 absorption spectra.

of the aldehyde function adjacent to the bromine only (**36**). After ring closure, the reactions were conducted as in the previous procedures. Compound **39** was dissolved into DMF and reacted with NBS in the dark to give **40**. Compound **40** easily reacted with 1-decyne under Sonogashira[36] reaction conditions to give good yields of the acetylene coupling product. However, when the alkyne group is linked in the α position, the reduction reaction becomes more difficult than that with the β-linked alkyne-fused thiophene compound.[29] Is the α-linked alkyne compound more effectively conjugated than the β-linked alkyne compound, which resulted in much harsher reaction conditions? More detailed study is needed before a conclusion can be reached. Reduction of the alkyne **41** by a Pd/C-catalyzed hydrogenation took 7 days, yielding the desired alkane. The one-side dialkyl-substituted fused thiophene compounds were reacted with NBS again to yield **43**. Halogen migration reactions have been previously reported[6,37] to be successful in moving the α-bromine to the β position in both thiophene and fused thiophene at −78 °C, followed by quenching with water. Although we made several attempts to repeat this reaction, almost all gave a mixture of 60−70% of **43** and 40−30% of **44** based on GC/MS and ^{1}H NMR. Finally, we found that, when the reaction was conducted at 0 °C in the presence of *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) to stabilize the anion, **43** could be converted to **44**. Although the yield is moderate, separation was much easier due to a minimized amount of the mixture of **43** and **44**. We then used Matzger's[6] coupling reaction procedure, followed by the ring closure procedure, to produce compound **46a**. We also prepared a tetradecanyl seven ring fused thiophene compound **46** when compound **26** (R = $C_{10}H_{21}$) was used as the starting material.

Characterization. The UV−vis absorption spectra obtained for the alkyl-substituted fused thiophenes in chloroform are shown in Figure 2, and the absorption maxima are summarized in Table 1. The spectra are shown in two plots for simplicity.

Although the optical properties (UV−vis) of fused thiophenes have been reported before, almost all of the reported spectral data are for unsubstituted fused ring systems.[9,24] It has not been possible to systematically study the effect of alkyl substitution on the absorption of fused thiophenes due to the unavailability of materials. Even though flexible alkyl chains were placed on the fused ring systems, the rigid π systems still demonstrated the same absorption patterns (in solution) as those of the unsubstituted versions. The vibronic fine structure of the absorption is evident for the compounds containing two to seven fused rings. Although the fused thiophene compounds demonstrate the expected red shifts as the number of fused rings is increased, when compared to their benzene analogues such as pentacene and the recently synthesized acenedithiophene,[4,10] the $\pi-\pi^*$ transitions are still significantly blue-shifted. **FT5** has its longest absorption at 362 nm, while pentacene has its at 575 nm.[10] Likewise, **FT7** has its longest absorption at 409 nm, while acenedithiophene has its at 762 nm.[4] Why do the fully conjugated fused thienothiophenes consistently display a significantly higher energy band when compared to that of the all carbon analogues? Matzger et al. recently stated that planarization of α-linked thiophenes acts to narrow the HOMO−LUMO gap, while adding sulfur atoms acts to widen it. This widening is thought to be due to the LUMO of α-linked thiophenes having the appropriate symmetry for interacting with the sulfur atoms introduced into fused thiophene structures, resulting in LUMO destabilization.[38]

Osuna et al.[8] have recently reported the HOMO−LUMO energy band gaps of unsubstituted **FT5** and **FT7**. When our results are compared with their report, it appears that alkyl substitution shifts the absorption to slightly lower energies. The unsubstituted **FT5** and **FT7** have their longest absorptions at 355 and 396 nm, respectively, whereas the substituted versions absorb at 362 and 409 nm, respectively. The additional 7 nm red shift in the substituted **FT5** should be due to the extra electron donation from the β-alkyl groups, while the 13 nm red shift in the substituted **FT7** could be a combination of both α- and β-alkyl group effects.

Stability and Solubility. The thermal behavior of the alkyl-substituted fused thiophene materials was investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). These results are shown in Figures 3 and 4. These data demonstrate that the substituted **FT4**, **FT5**, and **FT7** (note, **DMDC10FT7** is compound **46a**) have exceptional

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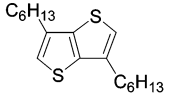
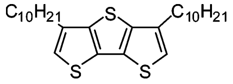
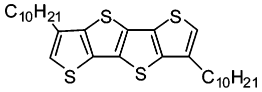
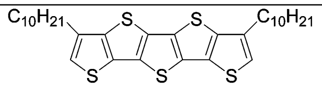
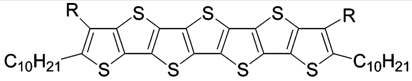
TABLE 1. Maximum UV−Vis Absorption of Fused Thienothiophene in $CHCl_3$ Solution

		structure	double bonds	absorption λ_{max} (nm)	$\Delta\lambda_{max}$ (nm)
FT2	**13**		3	267, 277, 287	
FT3	**19**		4	294, 309	22
FT4	**25**		5	308, 324, 338	29
FT5	**28**		6	318, 346, 362	24
FT7	**46**	 R= CH_3 and $C_{10}H_{21}$	8	368, 387, 409	47

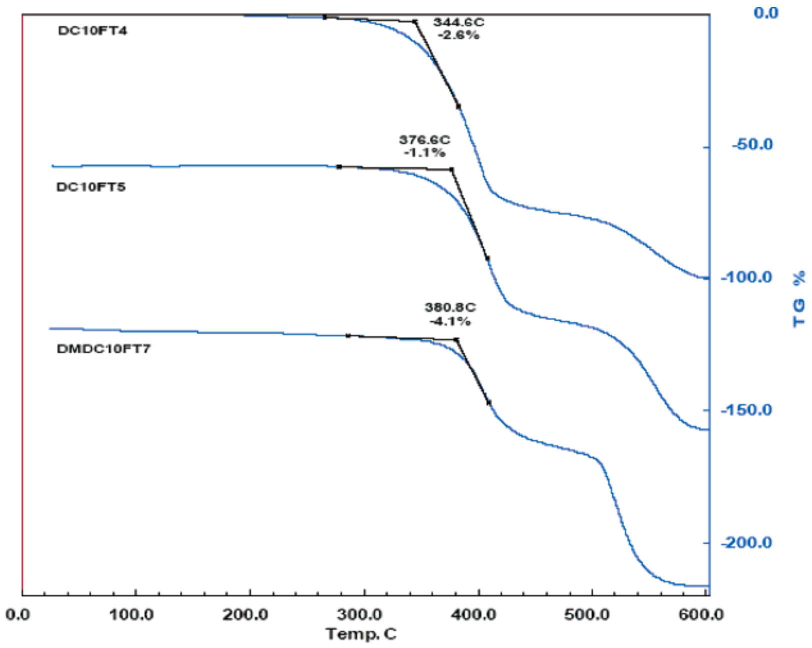


FIGURE 3. TGA results of **FT4**, **FT5**, and **FT7** in air.

thermal stability in air, even up to 340 °C. In the TGA traces, we noticed that there are two decompositions in the curves. We put all of the three compounds into a sublimation apparatus under nitrogen for tests. After heating them up to their decomposition temperature, all three compounds became dark, and no evidence of sublimation was observed.

Based on DSC analysis, **FT4** has a melting point at 112 °C, while **FT5** has a melting point at 109 °C, and **FT7** does not show an obvious melting point even when heated on a hot stage and observed using polarized light microscopy. None of these compounds have demonstrated any liquid−crystalline transition phases. The higher melting point of **FT4**, when compared to that with **FT5**, is most likely due to a different molecular symmetry.

All of the fused thiophene compounds exhibited some solubility in organic solvents. Due to their smaller ring size, **FT2** and **FT3** are the most soluble compounds in the series. Both are soluble in hexane, ethyl acetate, toluene, chlorobenzene, methylene chloride, and many other organic solvents. **FT4** and **FT5** are less soluble than **FT2** and **FT3**, but they still dissolve in hot hexane, methylene chloride, toluene, benzene, chlorobenzene, and other aromatic solvents. **FT7** has the poorest solubility

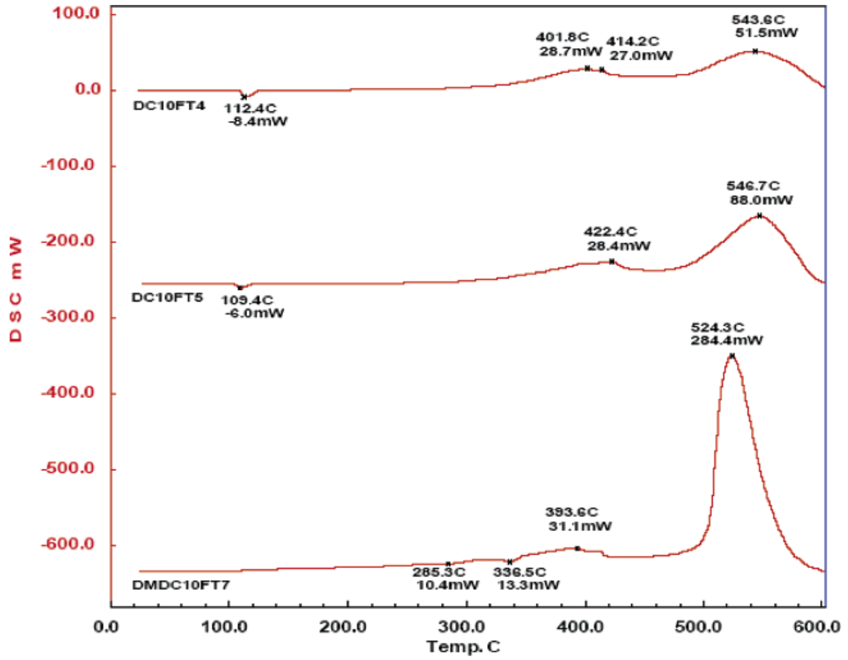


FIGURE 4. DSC results of **FT4**, **FT5**, and **FT7**.

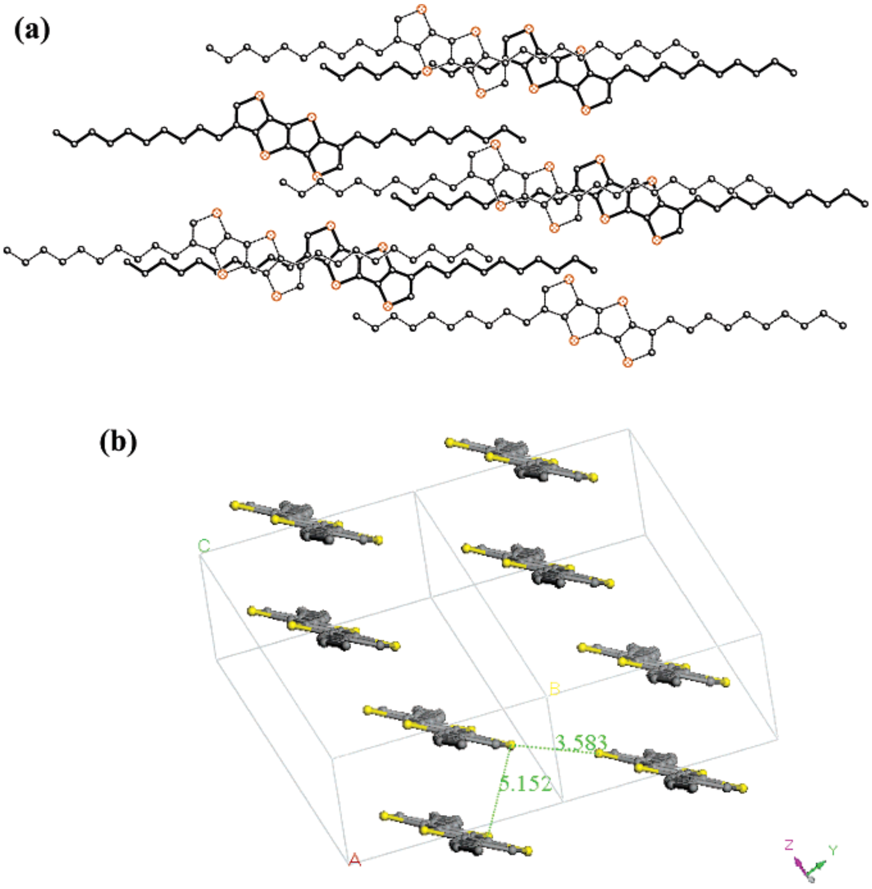


FIGURE 5. (a) Two layers of **FT4**. (b) Packing structure of **FT4** viewed through the tilted *BC* plane.

in the series. It is soluble in warm toluene, xylene, and chlorobenzene. All of these compounds can be processed into thin films through different solution methods.

Single-Crystal X-Ray. It was possible to obtain single crystals of **FT4** and **FT5** suitable for X-ray analysis by slow evaporation from a toluene solution. The detailed crystal-

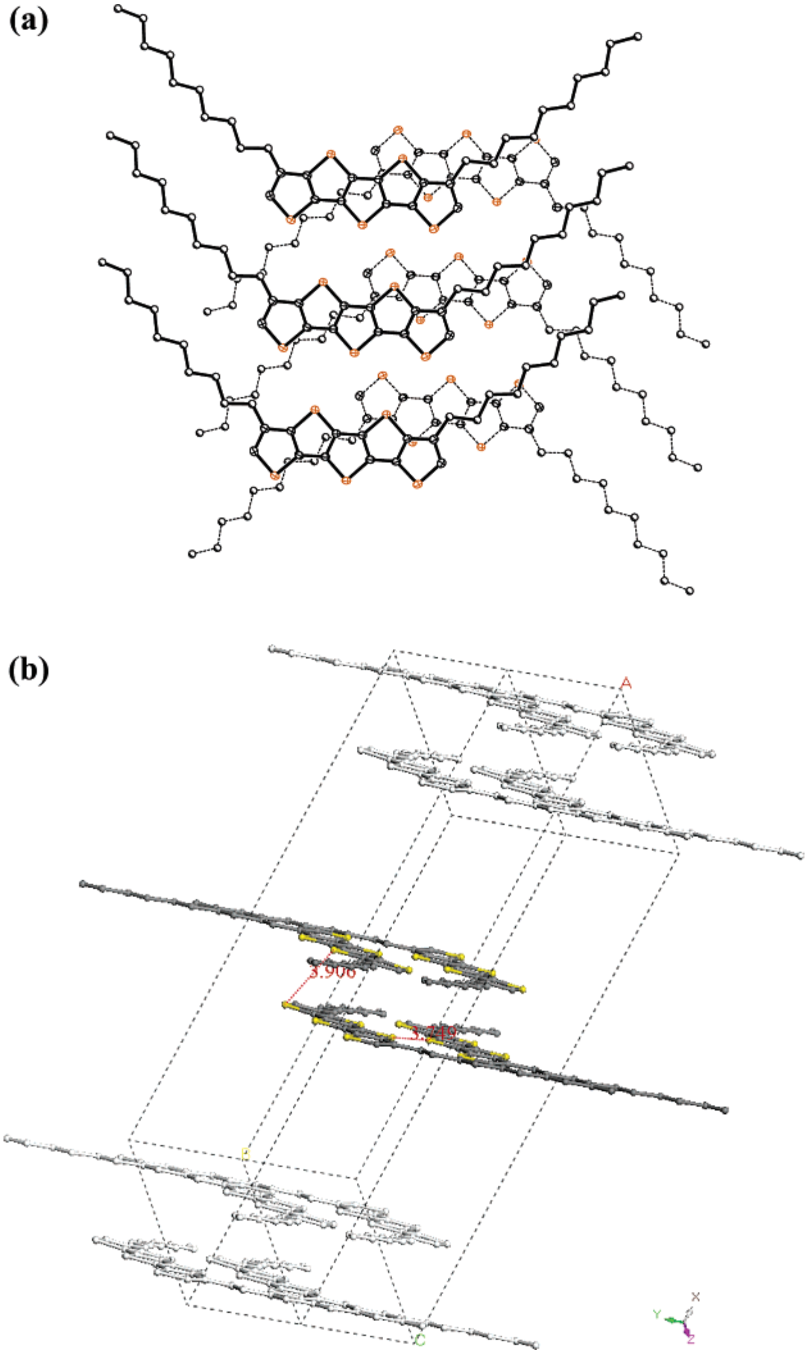


FIGURE 6. (a) Two layers of **FT5**. (b) Packing structure of **FT5** viewed through the tilted *AB* plane.

lographic data can be found in the Supporting Information. **FT4** and **FT5** showed different symmetry and packing motifs. **FT4** crystallizes in the *P*1 space group (triclinic crystal system), while **FT5** crystallizes in the *C*2/*c* space group (monoclinic crystal system). The crystal packings are illustrated in Figures 5 and 6. Unlike in the extensively studied polyaromatic hydrocarbon compounds[39−41]and the in previously reported packing patterns of unsubstituted **FT4** and α-substituted fused thiophenes, the β-substituted fused thiophenes do not show either the β-type or the herringbone-type of packing behavior.[6,11] Both **FT4** and **FT5** are very planar molecules that form layered structures. In the **FT4** crystal structure, the interlayer distance is found to be only 3.46(5) Å, and the closest distance between a sulfur atom in one molecule and a sulfur atom in an adjacent molecule in the same layer is 3.58(3) Å (Figure 5). This intralayer S−S distance is almost the same as that reported by Mazaki for the unsubstituted tetrathienoacene (3.482 Å).[11] Because we are interested in carrier mobility for the fused thiophene materials, we thought it would be relevant to consider the interlayer overlap between π systems. We used the shortest interlayer distance between S atoms on the fused core as a metric. In **FT4**, this

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[39] Gavezzotti, A.; Desiraju, G. R. *Acta. Crystallogr., Sect. B* **1988**, *44*, 427−434.

[40] Desiraju, G. R.; Gavezzotti, A. *Acta. Crystallallogr., Sect. B* **1989**, *45*, 473−482.

[41] Desiraju, G. R.; Gavezzotti, A. *J. Chem. Soc., Chem. Commun.* **1989**, 621−623.

distance was found to be 5.15(2) Å. This is relatively large compared to the interlayer distance of 3.46(5) Å, indicating that the interlayer overlap of the π systems is small. **FT4** seems to be packed in a ring-to-tail fashion with very little π−π orbital overlap. This particular packing behavior may be due to the much stronger intermolecular chain-to-chain interactions. The strong side-chain crystallization tendency appears to have pushed the ring to a position where the side-chain crystallization forces and π−π stacking tendency have reached a balance. The interlayer distance for **FT5** was found to be 3.44(5) Å, which is approximately the same as that for **FT4** and is not very different from the π−π distance of 3.52 Å reported by Matzger for unsubstituted pentathienoacene.[42] Within a single layer of **FT5**, the shortest intermolecular S−S distance is 3.74(9) Å. This is slightly longer than what was seen for unsubstituted and alkyl-substituted **FT4**. The most significant difference that is evident between the packing in **FT4** and **FT5** is the shortest S−S interlayer distance. In contrast to **FT4**, this distance is much shorter (3.90(6) Å vs 5.15(2) Å). By carefully examining the packing motif for **FT5** (Figure 6), one sees substantial π−π overlap, which greatly contributes to the shorter S−S distance between the molecules in different layers. In the unsubstituted pentathienoacene, the molecules within a stack seem to line up directly on top of each other.[42] In **FT5**, the addition of two long alkyl chains at the β positions of the pentathienoacence ring leads to a similarly π-stacked structure; however, the molecules in a stack are alternately rotated by 180° (Figure 6a). From a structure−property point of view, **FT5** has a different molecular symmetry and net dipole direction from that of **FT4**. Perhaps the orientation of the **FT5** molecules alternates between layers in order to minimize the dipolar interactions. Thus, for **FT5**, the tendency of the side chains to crystallize no longer appears to be the dominant force between molecules.

Due to the effect of the long side chains in the β position of these fused rings, these molecules are not packed as either a β-type or in a herringbone fashion. Layered structures were found for both of them. It is believed that this layered molecular packing is a more favorable morphology for electron transport. The short molecular layer distances indicate that all of the layers are packed even tighter than in poly(3-hexylthiophene) (3.8 Å).[43] It should be possible to modify the chain length so as to achieve more ring-to-ring overlap instead of ring-to-tail packing. Our results so far indicated that layered face-to-face packing can be achieved with the addition of β-alkyl substituents to the fused thiophene ring.

Conclusion

We have established a series of synthetic methods to obtain alkyl-substituted thienothiophenes with up to seven fused rings. By using these reaction methods, we have made both even and odd β- and α,β-alkyl-substituted fused thiophene compounds. Thermal characterization of these new fused thiophene compounds has demonstrated that they are very stable. UV−vis spectra show a large blue shift in absorption of all of the fused thiophenes when compared to that of their hydrocarbon counterparts. These larger band-gap materials are expected to have much better photo- and electrical stability than those of the hydrocarbon series. Since all of the compounds have long alkyl substituents, they exhibit good solubility in common organic solvents. These compounds may be able to be processed through solution deposition methods such as ink-jet printing and solution drop casting. Single-crystal X-ray structures of **FT4** and **FT5** demonstrated that their molecular packing behaviors are different from previously reported data for the unsubstituted materials. Layered molecular structures, instead of a β-type or a herringbone packing motif, have been observed in both **FT4** and **FT5**. These facts lead us to believe that adding β-alkyl substituents should benefit electron mobility due to a more ideal molecular arrangement. We are actively characterizing these new compounds and have already found some “odd−even” effects in our **FT4** and **FT5** compounds. We will continue to report our synthesis, characterization, and electrical measurements as they become available.

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Supporting Information Available: The detailed experimental section, all ^{1}H NMR, ^{13}C NMR spectra, selected GC/MS results, and X-ray data are available. This material is available free of charge via the Internet at http://pubs.acs.org.

JO061853Y

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[42] Zhang, X.; Johnson, J. P.; Kampf, J. W.; Matzger, A. J. *Chem. Mater.* **2006**, *18*, 3486−3488.

[43] Marsella, J. M.; Wang, Z.; Reid, J. R.; Yoon, K. *Org. Lett.* **2001**, *3*, 885−887 (Supporting Information).