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# Diels–Alder Reaction of 1,3-Diarylbenzo[*c*]furans with Thiophene *S,S*-Dioxide/Indenone Derivatives: A Facile Preparation of Substituted Dibenzothiophene *S,S*-Dioxides and Fluorenones

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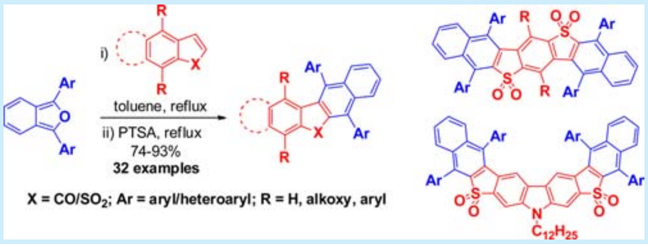
*Supporting Information*

**ABSTRACT:** One pot syntheses of substituted dibenzothiophene *S,S*-dioxides and fluorenones were successfully achieved by Diels–Alder reaction of benzo[*c*]furans with thiophene *S,S*-dioxides and indenones, respectively. Photophysical properties of representative seven- and nine-membered dibenzothiophene *S,S*-dioxide acenes were also reported.



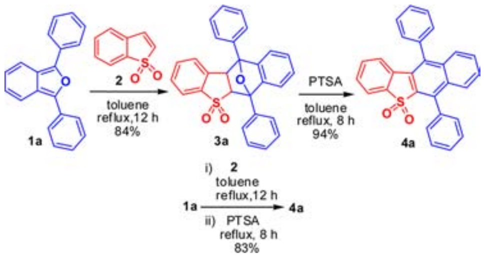
Dibenzothiophene[1] and fluorenone-based[2] $\pi$-conjugated materials have attracted renowned interest due to their promising applications in the area of organic electronics. Barbarella et al. first demonstrated that an introduction of one or more thiophene *S,S*-dioxide unit into the conjugated oligothiophene backbone provides a considerable reduction of HOMO–LUMO band gap value as well as an enhancement in the electron affinity compared to the parent oligothiophenes.[3] The oligothiophene *S,S*-dioxide also displayed a better solid-state photoluminescence efficiency.[4] The greater fluorescence efficiency and electron-transport properties of the dibenzothiophene *S,S*-dioxide-based materials[5] prompted chemists to undertake a comprehensive study on these compounds.[6−8] Perepichka et al. extensively utilized the dibenzothiophene *S,S*-dioxide unit as material for dual-fluorescence,[7a] strong solvatochromism,[7b] and high luminescence efficiency[7c] by incorporating into the main chain of oligofluorene. Recently, Yang and co-workers successfully synthesized alcohol-soluble amino-functionalized polyfluorene-tethered dibenzothiophene *S,S*-dioxides and explored their applications in polymer light emitting diodes (PLEDs) and polymer solar cells (PSCs).[8]

Oligo- and polyfluorenes have been explored as OLEDs with high quantum efficiencies.[9] To overcome the stability issue of fluorenes,[10] 9,9-dialkylfluorenes are being explored.[11] Recently, Goel and co-workers reported the donor–acceptor-type fluorene- and fluorenone-based small molecules as stable blue light emitters.[12] The Diels–Alder reaction is one of the ubiquitous reactions in organic synthesis and used for construction of polycyclic aromatics.[13] Over the years, the benzo[*c*]furan analogues were being exploited as a dienes in the Diels–Alder reactions to synthesize complex $\pi$-conjugated acenes.[14]

Our aim is to explore the synthetic utility of 1,3-disubstituted benzo[*c*]furans[15] as a diene in the Diels–Alder reaction to prepare $\pi$-conjugated dibenzothiophene *S,S*-dioxide and fluorenone derivatives. Recently, Iniesta and co-workers[16] achieved the preparation of dibenzothiophene *S,S*-dioxides through Diels–Alder reaction of benzo[*b*]thiophene *S,S*-dioxide and tetraphenylthiophene *S*-oxide. They have also carried out the Diels–Alder reaction of benzo[*b*]thiophene *S,S*-dioxide with dienes such as substituted butadiene, furan, cyclopentadiene, and tetracyclone to afford the respective adducts in moderate yields. As a representative case, the Diels–Alder reaction of 1,3- diphenylbenzo[*c*]furan **1a** with benzo[*b*]thiophene *S,S*-dioxide **2**[17] in toluene at reflux for 12 h afforded corresponding adduct **3a** in 84% yield.

Subsequent aromatization of the adduct **3** using *p*-toluenesulfonic acid (PTSA) led to the formation of the expected benzo[*d*]naphtho[*b*]thiophene *S,S*-dioxide **4a** in 83% yield. The Diels–Alder reaction of benzo[*c*]furan **1a** with **2** followed by aromatization without the isolation of intermediate adduct slightly improved the yield of **4a** (Scheme 1 and the Supporting Information). The structure of thiophene *S,S*-oxide **4a** was confirmed by a single-crystal X-ray analysis.[18]

**Scheme 1. Synthesis of Benzo[*b*]naphtho[*d*]thiophene *S,S*-Dioxide 4a**



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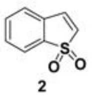
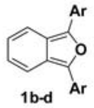
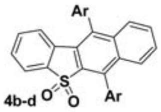
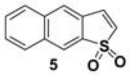
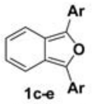
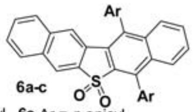
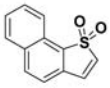
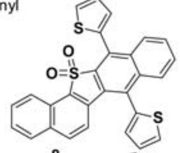
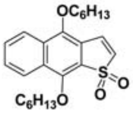
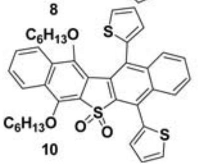
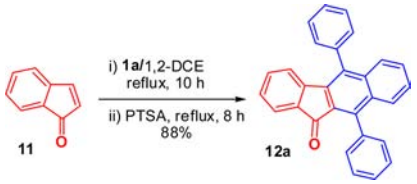
### Table 1. Synthesis of Dibenzothiophene *S*,*S*-Dioxides

| entry | substrate | benzo[*c*]furan | product[a] | yield (%)[b] |
|---|---|---|---|---|
| 1 | <br>**2** | <br>**1b-d**<br>**1b** Ar = *p*-tolyl<br>**1c** Ar = *p*-anisyl<br>**1d** Ar = 2-thienyl | <br>**4b-d**<br>**4b** Ar = *p*-tolyl<br>**4c** Ar = *p*-anisyl<br>**4d** Ar = 2-thienyl | 78<br>82<br>80 |
| 2 | <br>**5** | <br>**1c-e**<br>**1c** Ar = *p*-anisyl<br>**1d** Ar = 2-thienyl<br>**1e** Ar = 5-hexyl-2-thienyl | <br>**6a-c**<br>**6a** Ar = *p*-anisyl<br>**6b** Ar = 2-thienyl<br>**6c** Ar = 5-hexyl-2-thienyl | 84<br>80<br>76 |
| 3 | <br>**7** | **1d** | <br>**8** | 81 |
| 4 | <br>**9** | **1d** | <br>**10** | 75 |

[a]Diels–Alder reaction was allowed to reflux in toluene until the disappearance of furan (~12 h), and for aromatization (PTSA) it was refluxed until disappearance of the adduct (~10 h) was noted. [b]Isolated yield by column chromatography.

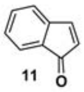
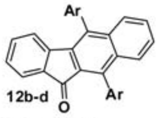
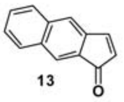
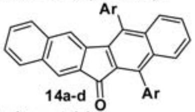
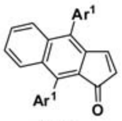
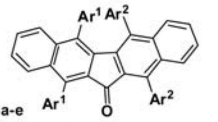
### Scheme 2. Diels–Alder Reaction of Indenone 11 with Furan 1a



Inspired by this result, the one-pot syntheses of dibenzothiophene *S*,*S*-dioxides **4b–d**, **6a–c**, **8**, and **10** have been successfully achieved in good to excellent yields (Table 1). The Diels–Alder reaction of benzo[*c*]furans **1b–d** with benzo[*b*]thiophene *S*,*S*-dioxide **2** followed by aromatization afforded benzo[*d*]naphtho[*b*]thiophene *S*,*S*-dioxides **4b–d** in good yields (entry 1). Under identical conditions, naphtho[*b*]thiophene *S*,*S*-dioxide **5** reacts with benzo[*c*]furans **1c–e** to furnish dinaphtho[*b*:*d*]thiophene *S*,*S*-dioxides **6a–c** in 76–84% yields (entry 2). Interestingly, the bent-naphtho[*b*]thiophene *S*,*S*-dioxide **7** also underwent smooth Diels–Alder reaction followed by aromatization to give dinaphtho[1,2-*b*:2′,3′-*d*]thiophene *S*,*S*-dioxide **8** in 81% yield (entry 3). The electron-rich bis(hexyloxy)dinaphtho[*b*:*d*]thiophene *S*,*S*-dioxide **9** successfully participated in the one-pot synthesis to give tetrasubstituted five-membered acene **10** in 75% yield (entry 4).

We next investigated the Diels–Alder reaction of benzo[*c*]-furans with a range of indenones. It should be noted that the indenone **11** and benzo[*b*]thiophene *S*,*S*-dioxide **2** have similar motifs, differing only at the C-1 position. To our delight, indenone **11**[19] upon Diels–Alder reaction with furan **1a** in 1,2-dichloroethane (DCE) at reflux for 10 h followed by aromatization furnished diphenylbenzo[*b*]fluorenone **12a** in 88% yield (Scheme 2).

### Table 2. Synthesis of Substituted Fluorenones

| entry | substrate | benzo[*c*]furan | product | yield (%)[c] |
|---|---|---|---|---|
| 1[a] | <br>**11** | **1b/1d/1e** | <br>**12b-d**<br>**12b** Ar = *p*-tolyl<br>**12c** Ar = 2-thienyl<br>**12d** Ar = 5-hexyl-2-thienyl | 93<br>88<br>86 |
| 2[a] | <br>**13** | **1b &1d-f** | <br>**14a-d**<br>**14a** Ar = *p*-tolyl<br>**14b** Ar = 2-thienyl<br>**14c** Ar = 5-hexyl-2-thienyl<br>**14d** Ar = 1-naphthyl | 87<br>85<br>82<br>81 |
| 3[b] | <br>**15a-b**<br>**15a** Ar$^1$ = phenyl<br>**15b** Ar$^1$ = *p*-anisyl | **1a-d** | <br>**16a-e**<br>**16a** Ar$^1$, Ar$^2$ = phenyl<br>**16b** Ar$^1$ = phenyl, Ar$^2$ = *p*-tolyl<br>**16c** Ar$^1$ = phenyl, Ar$^2$ = *p*-anisyl<br>**16d** Ar$^1$ = phenyl, Ar$^2$ = 2-thienyl<br>**16e** Ar$^1$, Ar$^2$ = *p*-anisyl | 79<br>81<br>84<br>76<br>81 |

[a]The Diels–Alder reaction was carried out in 1,2-DCE at reflux until disappearance of furan in TLC (10 h), and for aromatization it was refluxed until adduct disappearance (9 h) was noted. [b]Reaction was carried out in toluene for 14 h, and aromatization was allowed for 12 h. [c]Isolated yield by column chromatography.

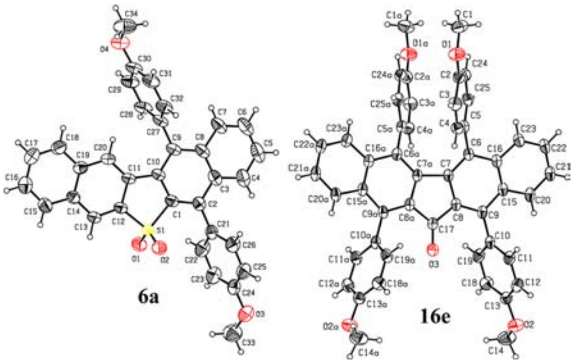
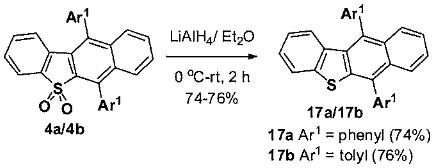


**Figure 1.** Single-crystal X-ray structures of **6a** and **16e**.

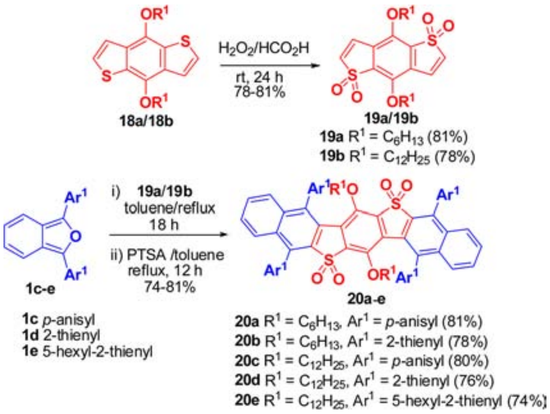
Next, the indenone **11**, naphtho[*b*]indenone **13**, as well as the diaryl-substituted naphtho[*b*]indenone **15a,b** also participated in the Diels–Alder reaction followed by aromatization to afford the corresponding benzo/naphthofluorenones **12b–d**, **14a–d**, and **16a–e** in excellent yields (Table 2). It is worth mentioning that the indenones **11** and **13** require lower temperature than that of diaryl substituted indenone **15a,b**. The structures of thiophene *S*,*S*-dioxide **6a** and fluorenone **16e** were confirmed by single-crystal X-ray analyses (Figure 1).[18]

After demonstrating the preparation of a variety of benzo/naphtho dibenzothiophene *S*,*S*-dioxides and fluorenones by the Diels–Alder reaction of 1,3-diarylbenzo[*c*]furans, we next initiated the reduction[1e] of dibenzothiophene *S*,*S*-dioxides. As a representative case, diphenyldibenzothiophene *S*,*S*-dioxide **4a** upon reduction with lithium aluminum hydride (LAH) in diethyl ether at 0 °C to rt for 2 h afforded diphenyldibenzothiophene derivative **17a** in 74% yield (Scheme 3). Similarly,

### Scheme 3. Preparation of Dibenzothiophene Derivatives 17a,b



### Scheme 4. Synthesis of Seven-Membered Thiophene *S,S*-Dioxide Acenes 20a–e

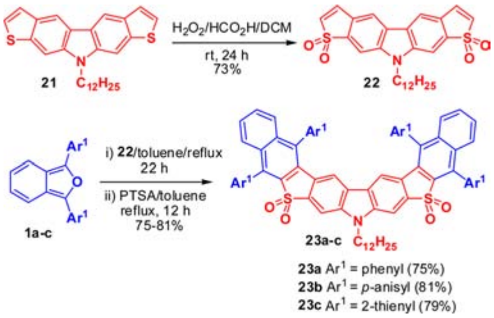


dibenzothiophene *S,S*-dioxide **4b** also converted into the corresponding dibenzothiophene **17b** in good yield.

To explore the scope further, synthesis of higher acenes containing thiophene *S,S*-dioxide units has been initiated. The bis(hexyloxy)benzodithiophene and *N*-dodecyldithieno carbazole derivatives have been synthesized and incorporated in polymers due to their potential optical properties.[20] Hence, the required bis(hexyloxy)benzodithiophene *S,S*-dioxide **19a/19b** was prepared by the routinely used HCO$_2$H/H$_2$O$_2$ procedure.[17] Gratifyingly, the one-pot synthesis of hexaaryl-substituted thiophene *S,S*-dioxide fused seven member acenes **20a–e** have been successfully achieved in good yields (Scheme 4).

Next, we began to construct more complex and challenging higher acenes containing carbazole-fused thiophene *S,S*-dioxides. The Diels–Alder reaction of diphenylbenzo[*c*]furan **1a** with thiophene *S,S*-dioxide **22** followed by adduct bridge cleavage furnished dithienocarbazole-fused nine-membered acene **23a** in 75% yield. Finally, the anisyl/thienyl-tethered dithienocarbazole-fused nine-membered acenes **23b/23c** have also been achieved using a one-pot Diels–Alder synthetic strategy (Scheme 5).

### Scheme 5. Synthesis of Nine-Membered Thiophene *S,S*-Dioxide Acenes 23a–c



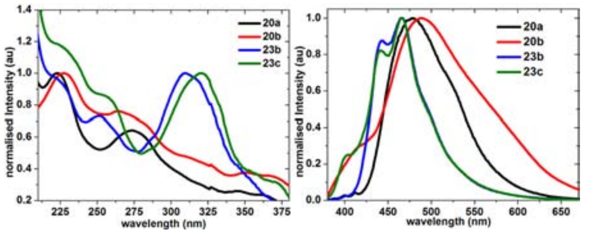


**Figure 2.** Absorption and emission spectra of thiophene *S,S*-dioxides **20a**, **20b**, **23b**, and **23c**.

**Table 3. Photophysical Studies of Thiophene *S,S*-Dioxides**

| entry | product | absorption[a] $\lambda_{\max(\text{abs})}$ (nm) | emission[a,b] $\lambda_{\max(\text{em})}$ (nm) | Stokes shift[c] (cm$^{-1}$) | quantum yield $\Phi$[a] |
|---|---|---|---|---|---|
| 1 | **20a** | 275 | 478 | 15443 | 0.210 |
| 2 | **20b** | 265 | 488 | 17244 | 0.019 |
| 3 | **20c** | 274 | 479 | 15619 | 0.180 |
| 4 | **20d** | 266 | 486 | 17017 | 0.018 |
| 5 | **23b** | 382 | 467 | 4764 | 0.054 |
| 6 | **23c** | 392 | 466 | 4051 | 0.045 |

[a] Recorded in CH$_3$CN at 25 °C. [b] Excited at the longest wavelength of the absorption maxima. [c] Stokes shift = $\lambda_{\max(\text{abs})} - \lambda_{\max(\text{em})}$ (cm$^{-1}$).

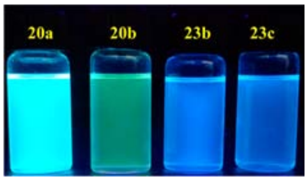


**Figure 3.** Luminescence color upon illumination at 365 nm.

**Table 4. Fluorescence Lifetimes of 20a, 20b, 23b, and 23c***

| compd | $\tau_1$ (ps) | $\tau_2$ (ns) | $\tau_3$ (ns) | A1 (%) | A2 (%) | A3 (%) | $\chi^2$ |
|---|---|---|---|---|---|---|---|
| **20a** | | | 1.20 | | | 100 | 1.148 |
| **20b** | 43.30 | 0.25 | 0.90 | 16.13 | 61.13 | 22.74 | 0.943 |
| **23b** | | 1.50 | 3.39 | | 10.84 | 89.16 | 1.081 |
| **23c** | | 0.627 | 1.86 | | 25.97 | 74.03 | 1.226 |

[*] Measured using the TCSPC technique and excited at 370 nm and monitored at their respective emission maximum.

The optical properties of the novel thiophene *S,S*-dioxides **20a**, **20b**, **23b**, and **23c** were investigated by UV–vis and fluorescence spectroscopy (Figure 2, Table 3). The absorption spectra of thiophene *S,S*-dioxides **23b** and **23c** shifted to lower energies compared to the compounds **20a** and **20b**. Figure 3 shows the emission color of **20a**, **20b**, **23b**, and **23c** in acetonitrile upon illumination at 365 nm. The thiophene *S,S*-dioxides **20a** and **20b** exhibited broad emission band and larger Stokes shift compared to the thiophene *S,S*-dioxides **23b** and **23c** (Table 3). The fluorescence quantum yield was measured using quinine sulfate as a standard (0.1 N H$_2$SO$_4$) $\Phi_f = 0.54$ at an excitation wavelength of 366 nm. It is worth mentioning that among thiophene *S,S*-dioxide-based acenes, compounds **20a** and **20c** displayed much enhanced fluorescence quantum yields (Table 3).

Next, the time-correlated single photon counting (TCSPC) measurement of thiophene *S,S*-dioxides **20a**, **20b**, **23b**, and **23c** were carried out in acetonitrile at room temperature (Table 4 and the Supporting Information). It should be noted that the fluorescence lifetime decay of compounds **20a** and **20b** displayed single-exponential and triexponential behavior, while both **23b** and **23c** exhibited biexponential behavior (Table 4). The triexponential fluorescence lifetime decay of **20b** may be attributed to the different conformational isomers visualized through the restricted rotation of thiophene units. However, the VT $^1$H NMR spectra of **20b** did not provide any evidence for such conformational isomers (see the Supporting Information). Further photophysical studies on **20b** and other structurally related compounds may provide a possible reason for triexponential/biexponential behavior of these compounds.

In summary, we have successfully exploited the Diels−Alder reaction of benzo[*c*]furans with annulated thiophene *S*,*S*-dioxides and indenones that provides a new method for the preparation of $\pi$-conjugated thiophene *S*,*S*-dioxides and fluorenones. Synthesis and photophysical properties of seven- as well as nine-membered acenes and also the fluorescence lifetime decay of selected thiophene *S*,*S*-dioxides have been carried out. Further studies toward the synthesis and optical application of thiophene *S*,*S*-dioxide-based hetero acenes are in progress.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental procedure, copies of NMR spectra, and X-ray crystallographic data of **4a**, **6a**, and **16e** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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## ■ DEDICATION

This paper is dedicated to Prof. Ganesh Pandey on the occasion of his 60th birthday.

## ■ REFERENCES

(1) (a) Dong, S.-C.; Zhang, L.; Liang, J.; Cui, L.-S.; Li, Q.; Jiang, Z.-Q.; Liao, L.-S. *J. Phys. Chem. C* **2014**, *118*, 2375. (b) Jin, E.; Du, C.; Wang, M.; Li, W.; Li, C.; Wei, H.; Bo, Z. *Macromolecules* **2012**, *45*, 7843. (c) Jeong, S. H.; Lee, J. Y. *J. Mater. Chem.* **2011**, *21*, 14604. (d) Huang, T.-H.; Whang, W.-T.; Shen, J. Y.; Lin, J. T.; Zheng, H. *J. Mater. Chem.* **2005**, *15*, 3233. (e) Sirringhaus, H.; Friend, R. H.; Wang, C.; Leuninger, J.; Müllen, K. *J. Mater. Chem.* **1999**, *9*, 2095.

(2) (a) Lincker, F.; Heinrich, B.; Bettignies, R. D.; Rannou, P.; Pécaut, J.; Grévin, B.; Pron, A.; Donnio, B.; Demadrille, R. *J. Mater. Chem.* **2011**, *21*, 5238. (b) Rathnayake, H. P.; Cirpan, A.; Karasz, F. E.; Odoi, M. Y.; Hammer, N. I.; Barnes, M. D.; Lahti, P. M. *Chem. Mater.* **2007**, *19*, 3265. (c) Zhu, Y.; Kulkarni, A. P.; Jenekhe, S. A. *Chem. Mater.* **2005**, *17*, 5225. (d) Chen, C.-T.; Lin, J.-S.; Moturu, M. V. R. K.; Lin, Y.-W.; Yi, W.; Tao, Y.-T.; Chien, C.-H. *Chem. Commun.* **2005**, 3980.

(3) Barbarella, G.; Favaretto, L.; Zambianchi, M.; Pudova, O.; Arbizzani, C.; Bongini, A.; Mastragostino, M. *Adv. Mater.* **1998**, *10*, 551.

(4) Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Bongini, A.; Arbizzani, C.; Mastragostino, M.; Anni, M.; Gigli, G.; Cingolani, R. *J. Am. Chem. Soc.* **2000**, *122*, 11971.

(5) (a) Liu, J.; Hu, S.; Zhao, W.; Zou, Q.; Luo, W.; Yang, W.; Peng, J.; Cao, Y. *Macromol. Rapid Commun.* **2010**, *31*, 496. (b) Liu, J.; Zou, J.; Yang, W.; Wu, H.; Li, C.; Zhang, B.; Peng, J.; Cao, Y. *Chem. Mater.* **2008**, *20*, 4499. (c) Huang, T.-H.; Whang, W.-T.; Shen, J. Y.; Wen, Y.-S.; Lin, J. T.; Ke, T.-H.; Chen, L.-Y.; Wu, C.-C. *Adv. Funct. Mater.* **2006**, *16*, 1449.

(6) Moss, K. C.; Bourdakos, K. N.; Bhalla, V.; Kamtekar, K. T.; Bryce, M. R.; Fox, M. A.; Vaughan, H. L.; Dias, F. B.; Monkman, A. P. *J. Org. Chem.* **2010**, *75*, 6771.

(7) (a) King, S. M.; Perepichka, I. I.; Perepichka, I. F.; Dias, F. B.; Bryce, M. R.; Monkman, A. *Adv. Funct. Mater.* **2009**, *19*, 586. (b) Dias, F. B.; Pollock, S.; Hedley, G.; Pålsson, L.-O.; Monkman, A.; Perepichka, I. I.; Perepichka, I. F.; Tavasli, M.; Bryce, M. R. *J. Phys. Chem. B* **2006**, *110*, 19329. (c) Perepichka, I. I.; Perepichka, I. F.; Bryce, M. R.; Pålsson, L.-O. *Chem. Commun.* **2005**, 3397.

(8) Xiao, H.; Miao, J.; Cao, J.; Yang, W.; Wu, H.; Cao, Y. *Org. Electron.* **2014**, *15*, 758.

(9) (a) Marsitzky, D.; Müllen, K. In *Advances in Synthetic Metals, Twenty Years of Progress in Science and Technology*; Bernier, P., Lefrant, S., Bidan, G., Eds.; Elsevier: New York, 1999; p 1. (b) Mullen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, 1998. (c) Akcelrud, L. *Prog. Polym. Sci.* **2003**, *28*, 875.

(10) (a) Liu, L.; Qiu, S.; Wang, B.; Zhang, W.; Lu, P.; Xie, Z.; Hanif, M.; Ma, Y.; Shen, J. *J. Phys. Chem. B* **2005**, *109*, 23366. (b) List, E. J. W.; Guentner, R.; Freitas, P. S. D.; Scherf, U. *Adv. Mater.* **2002**, *14*, 374. (c) Bliznyuk, V. N.; Carter, S. A.; Scott, J. C.; Klärner, G.; Miller, R. D.; Miller, D. C. *Macromolecules* **1999**, *32*, 361.

(11) Cho, S. Y.; Grimsdale, A. C.; Jones, D. J.; Watkins, S. E.; Holmes, A. B. *J. Am. Chem. Soc.* **2007**, *129*, 11910.

(12) Goel, A.; Chaurasia, S.; Dixit, M.; Kumar, V.; Prakash, S.; Jena, B.; Verma, J. K.; Jain, M.; Anand, R. S.; Manoharan, S. S. *Org. Lett.* **2009**, *11*, 1289.

(13) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: New York, 1990.

(14) (a) Wang, T.; Han, J.; Zhang, Z.; Xu, B.; Huang, J.; Su, J. *Tetrahedron* **2012**, *68*, 10372. (b) Nishina, Y.; Kida, T.; Ureshino, T. *Org. Lett.* **2011**, *13*, 3960. (c) Kuninobu, Y.; Seiki, T.; Kanamaru, S.; Nishina, Y.; Takai, K. *Org. Lett.* **2010**, *12*, 5287. (d) Qu, H.; Chi, C. *Org. Lett.* **2010**, *12*, 3360. (e) Klassen, S. A.; Boehme, R.; Derrick, S. D.; Moock, K.; Baker, E. A.; Fogg, D. E.; Boeré, R. T.; Dibble, P. W. *Can. J. Chem.* **2009**, *87*, 738. (f) Paraskar, A. S.; Reddy, A. R.; Patra, A.; Wijsboom, Y. H.; Gidron, O.; Shimon, L. J. W.; Leitus, G.; Bendikov, M. *Chem.—Eur. J.* **2008**, *14*, 10639. (g) Rainbolt, J. E.; Miller, G. P. . *J. Org. Chem.* **2007**, *72*, 3020. (h) Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2006**, *71*, 4085. (i) Miller, G. P.; Briggs, J. *Org. Lett.* **2003**, *5*, 4203. (j) Dodge, J. A.; Bain, J. D.; Chamberlin, A. R. *J. Org. Chem.* **1990**, *55*, 4190. (k) Smith, J. G.; Fogg, D. E.; Munday, I. J.; Sandborn, R. E.; Dibble, P. W. *J. Org. Chem.* **1988**, *53*, 2942.

(15) (a) Sivasakthikumaran, R.; Nandakumar, M.; Mohanakrishnan, A. K. *J. Org. Chem.* **2012**, *77*, 9053. (b) Nandakumar, M.; Sivasakthikumaran, R.; Mohanakrishnan, A. K. *Eur. J. Org. Chem.* **2012**, 3647.

(16) Iniesta, J.; Matsumoto, T.; Thiemann, T. *J. Chem. Res.* **2008**, *2*, 109.

(17) Rademacher, P. M.; Woods, C. M.; Huang, Q.; Szklarz, G. D.; Nelson, S. D. *Chem. Res. Toxicol.* **2012**, *25*, 895.

(18) CCDC numbers for **4a**, **6a**, and **16e** are 997380, 997383, and 997450, respectively (see the Supporting Information).

(19) Hauser, F. M.; Zhou, M.; Sun, Y. *Synth. Commun.* **2001**, *31*, 77.

(20) (a) Wang, X.; Jiang, P.; Chen, Y.; Luo, H.; Zhang, Z.; Wang, H.; Li, X.; Yu, G.; Li, Y. *Macromolecules* **2013**, *46*, 4805. (b) Deng, Y.; Chen, Y.; Liu, J.; Liu, L.; Tian, H.; Xie, Z.; Geng, Y.; Wang, F. *ACS Appl. Mater. Interfaces* **2013**, *5*, 5741.