

# Materials Science inc. Nanomaterials & Polymers

# New Aryl-Substituted 2,2'-Bithiophenes: Synthesis, Optoelectronic Properties and DFT Studies

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Phenyl- and thien-2-yl-[2,2'-bithiophen]-5-yl)(thiophen-2-yl) methanones were synthesized by the condensation of 2-thienyldithioester with the corresponding methyl ketones followed by cyclization with 2-bromoacetylthiophene. Also, condensation of 2-thienyldithioester with methyl ketones followed by treatment with methyl iodide gave  $\beta$ -thien-2-yl- $\beta$ -methylthio- $\alpha$ , $\beta$ -unsaturated ketones, which reacted with the Simmons-Smith reagent to give corresponding 4-phenyl- and thien-2-yl-2,2'-bithiophenes. The optoelectronic properties of these bithiophene derivatives were studied by UV-Vis absorption, fluorescence spectroscopy and cyclic voltammetry. The

## Introduction

Organic electronics applications have stimulated much industrial and academic research into the synthesis and development of new materials incorporating  $\pi$ -conjugated organic small molecules and polymers. Thiophene derivatives, oligo- and polythiophenes are an important class of molecules which have been synthesized and have shown numerous applications in such materials and devices.<sup>[1-3]</sup> Oligo- and polythiophenes can be synthesized by various transition metal (TM)-catalyzed crosscoupling reactions. Using such C-C bond forming reactions, molecular building blocks containing pre-constructed thiophene units can be readily linked to suitable cross-coupling partners (e.g. alkenes, alkynes, and arenes), yielding  $\pi$ conjugated thiophene oligomers and polymers.<sup>[4-6]</sup> Many oligo-/polythiophenes which have been reported in the literature<sup>[2,7]</sup> are linear polythiophenes with alkyl chains<sup>[8–11]</sup> and/or with polar functional groups as substituents.<sup>[12-17]</sup> Linear polythiophenes with aryl substituents however are rare.<sup>[14]</sup> Also, polymers of 3,2':4',3"-terthiophene,<sup>[18]</sup> 2,2':5',2"-terthiophene<sup>[12]</sup> and 2,2':3',2"-terthiophene<sup>[19]</sup> are known but not with 2,2':4',2"terthiophene, the latter of which would give hyperbranched polythiophenes, which have not been extensively reported in the literature.<sup>[20-25]</sup> The number of commercially-available or lowest-energy conformations of these new compounds in the ground and first excited states, the electronic origins of their UV-Vis absorption and fluorescence emission bands, and related frontier molecular orbital (FMO) properties were elucidated by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. Furthermore, these aryl-substituted bithiophenes were treated with anhydrous ferric chloride to undergo oxidative polymerization, and the fluorescence properties of the resulting polymeric products are also reported herein.

easily synthesized thiophene building blocks however for further exploiting the potential of thiophene-based molecules is relatively limited. The classical methods for synthesizing thiophene building blocks include the Paal-Knorr<sup>[26a-c]</sup> and Gewald<sup>[27a,b]</sup> methods and also a variety of other more recent methods<sup>[28a-l]</sup>

Based upon these backgrounds, and upon our earlier reported synthetic approach to new thiophene building blocks by a dithioester-involved cyclization methodology<sup>[29]</sup> whereby 4-phenyl- and 4-thienyl-substituted 2,2'-bithio-phenes 4a-b and the corresponding carbonyl group-linked 2-thienyl derivatives 6a-b could be targeted and their optical- and physicochemical properties studied. The new 2,2'-bithiophene derivatives reported in this work not only allows for some structureproperty relationships for 4-aryl-functionalized 2,2'-bithiophenes to be further understood, but also offers synthetic entry to a different class of hyperbranched polythiophenes through oxidative polymerization of thienyl-substituted bithiophenes 4a and the 2,2':4',2"-terthiophene 4b as precursors. Herein, our designed synthetic targets 4a/b and 6a/b, Scheme 1) represent a class of thiophene oligomers or building blocks, for which preliminary investigations have revealed some intriguing structural and electronic properties.

# **Results and Discussion**

## Synthesis

A Claisen-type condensation reaction of methyl ketones **1a** or **1b** with 2-thienyl dithioester (**2**) in the presence of sodium hydride in DMF, followed by treatment with methyl iodide formed inseparable mixtures of the corresponding *E* and *Z* isomers of  $\beta$ -thien-2-yl- $\beta$ -methylthio- $\alpha$ , $\beta$ -unsaturated ketones **3a** and **3b**, respectively, in 82–84% yields. Reaction of **3a** or

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Scheme 1. Synthesis of bithiophene derivatives 4 a/b and 6 a/b.

3b with Simmons-Smith reagent, prepared by refluxing diiodomethane and zinc-copper couple in dichloromethane, afforded 4-phenyl- or thien-2-yl-2,2'-bithiophenes 4a or 4b respectively in 45–55% yields.<sup>[29,30a-c]</sup> The lower yields of thiophenes 4a and 4b can be explained by the fact that only the Z isomers of 3a or 3b reacted with the Simmons-Smith reagent, whilst the interconversion of E and Z isomers is not efficient under the reaction conditions. On the other hand, condensation of methyl ketones 1a (R=Ph) or 1b (R=2-thienyl) with 2 in the presence of sodium hydride in DMF followed by treatment with 2bromo-acetylthiophene (5) gave the corresponding 4-phenyland thien-2-yl-[2,2'-bithiophen]-5-yl)(thiophen-2-yl)methanones 6a or 6b, respectively, in 80-85% yields (Scheme 1).<sup>[29]</sup> The molecular structures of these all compounds were characterized by IR, NMR and HRMS analyses (see the ESI for details).

#### **Electronic Absorption and Emission Properties**

The electronic absorption properties of compounds 4a/b and 6a/b were investigated by UV-Vis absorption spectroscopy. Their absorption spectra recorded in chloroform solution and detailed photophysical data are provided in Figure 1 and Table S1 in the ESI. To understand the origins of the electronic transitions in the experimentally determined UV-Vis absorption spectra, TD-DFT calculations were performed on 4a/b and 6a/ b. In the calculations, the ground-state geometries of the compounds were first optimized using the M06-2X functional<sup>[31]</sup> with the 6-31G(d) basis set to find their lowest-energy conformations. These structures were then subjected to singlepoint TD-DFT analyses using the B3LYP functional<sup>32</sup> and a relatively large basis set, 6-311+G(d,p) to obtain simulated UV-Vis spectra, which are shown in Figure 1 as well for comparison purposes. As can be seen in Figure 1, the spectrum of 4a shows one absorption band at 312 nm in its experimental UV-Vis spectrum, which agrees very well with the TD-DFT calculated HOMO  $\rightarrow$  LUMO transition at 316 nm. Compared with the spectrum of 6a bithiophene 4a lacks the thiophene-2carbonyl group, which results in a hypsochromic shift relative



to **6a** by 17 nm. Compound **4b** shows an absorption maximum at 285 nm along with a low-energy shoulder band around 329 nm. According to the TD-DFT analysis, the shoulder band is due to the HOMO  $\rightarrow$  LUMO transition (calculated at 326 nm) and the other band is ascribed to a combination of HOMO-1  $\rightarrow$ LUMO and HOMO  $\rightarrow$  LUMO + 1. Replacing the phenyl group in **4a** by a 2-thienyl group (as in **4b**) causes the HOMO  $\rightarrow$  LUMO band of **4b** to shift hypsochromically by 27 nm relative to that of 4a in the experimental observation. Compound 6a exhibits two major absorption bands at 378 nm and 295 nm in its experimental spectrum, which reasonably agree with the TD-DFT calculated two most intensive transition bands at 384 and 300 nm respectively. The lowest-energy band is due to the HOMO  $\rightarrow$  LUMO transition, while the other arises from the combination of HOMO  $\rightarrow$  LUMO+1 and HOMO-2  $\rightarrow$  LUMO. The calculated HOMO  $\rightarrow$  LUMO transition (384 nm) appears to be slightly red-shifted by 7 nm relative to the experimental value (377 nm). The discrepancy can be accounted for by that the TD-DFT calculations only took the lowest-energy conformer of 6a into consideration, whereas the actual molecule of 6a in solution can adopt multiple conformations, most of which are less  $\pi$ -conjugated than the optimized geometry. Similarly, compound 6b shows two UV-Vis absorption bands at 376 nm and 301 nm in its experimental spectrum, which match the two significant transitions at 397 nm and 309 nm predicted by the TD-DFT calculations. Herein the lower-energy band is assigned to the HOMO  $\rightarrow$  LUMO transition and the other is due to HOMO  $\rightarrow$  LUMO+1 and HOMO-2  $\rightarrow$  LUMO. As with 6a, the TD-DFT calculated UV-Vis absorption bands for compound 6b are slightly lower in energy than the experimental data as a result of the consideration of only the optimized conformational structure of **6b** in the calculations.

The electronic emission properties of compounds 4a/b and 6a/b in chloroform were also characterized by fluorescence spectroscopy. As shown in Figure 2, compounds 6a and 6b give broad and relatively weak emission bands at 463 nm and 446 nm respectively. Comparatively, the maximum emission bands of 4a and 4b are significantly shorter in wavelength and greater in intensity than those of 6a/b; compound 4a shows an emission peak at 386 nm and 6b at 390 nm. To understand the fluorescence properties, the first excited singlet states  $(S_1)$ of compounds 4a/b and 6a/b were simulated by TD-DFT calculations, wherein the optimized S<sub>1</sub> geometries were first calculated by the B3LYP/6-31G(d) level of theory and then the vertical emission energies from  $S_1$  to  $S_0$  were computed at the B3LYP/6-311 + G(d,p) level based on the optimized geometries. The TD-DFT predicted vertical emission energy for 4a is 3.20 eV (387 nm, f=0.3365) and for **4b** it is 3.09 eV (401 nm, f=0.1682), both of which are in good agreement with the experimentally observed fluorescence emission wavelengths. The origins of these bands are assigned to the LUMO  $\rightarrow$  HOMO transition according to the TD-DFT analysis. For the carbonylcontaining compounds 6a and 6b, however, the TD-DFT predicted LUMO  $\rightarrow$  HOMO transitions are 1.63 eV (761 nm, f =0.0011) and 1.65 eV (753 nm, f=0.0027) respectively, which do not match their experimentally observed emission bands. Rather, the fluorescence peaks of 6a and 6b agree well with





Figure 1. UV-Vis absorption spectra of compounds 4a/b and 6a/b measured in chloroform at room temperature (plotted as blue colour traces) in comparison with TD-DFT calculated UV-Vis spectra (as bar graphs in red colour, calculated at the M06-2X/6-31G(d)//B3LYP-6311 + G(d,p) levels).



**Figure 2.** Fluorescence spectra of compounds **4a/b** and **6a/b** measured in chloroform at room temperature. Excitation wavelengths ( $\lambda_{ex}$ ): **4a** (378 nm), **4b** (375 nm), **6a** (318 nm), and **6b** (286 nm).

the LUMO  $\rightarrow$  HOMO–1 transitions calculated by the TD-DFT analysis.

Table 1 reveals the key structural parameters of compounds 4a/b and 6a/b in the ground singlet (S<sub>0</sub>) and the first excited







Figure 3. Contours (isovalue = 0.032) and energies of the FMOs for 4a/b and 6a/b in the first excited singlet state (S<sub>1</sub>) calculated at the B3LYP/6-31G(d)//B3LYP/6-311 + G(d,p) levels.

singlet (S<sub>1</sub>) states. The structures of **4a** and **4b** are slightly deviated from planarity in the S<sub>0</sub> state, with twist angles between the aryl rings ( $\theta_1$  and  $\theta_2$ ) in the range of *ca*. 20 to 30°. Upon vertical excitation, the shapes of **4a** and **4b** become flattened as indicated by the considerably reduced  $\theta_1$  and  $\theta_2$  values. Along with the conformational changes, **4a** and **4b** gain a higher degree of  $\pi$ -electron delocalization as evidenced by the significant shortening of the two  $\sigma$  bonds (C1-C2 and C3-C4) bridging the aryl rings. The calculated frontier molecular orbitals (FMOs) of **4a** and **4b** (Figure 3) in their S<sub>1</sub> state reveal a large degree of spatial overlap between the HOMO and LUMO, hence suggesting that the LUMO  $\rightarrow$  HOMO transition would be favoured in their emission behaviour.

It can be noted that the linearly  $\pi$ -conjugated segments of **6** a/b, namely, the phenyl-thienyl-thienyl of **6** a and the thienyl-thienyl-thienyl branches of **6** b, become more co-planar when excited from the S<sub>0</sub> to S<sub>1</sub> states (see the changes in their  $\theta_1$  and  $\theta_2$  values in Table 1). On the other hand, the thiophene-2-carbonyl or benzoyl group rotates from a moderate twist angle (ca. 40°) to a nearly perpendicular orientation with respect to the central thienyl unit of the molecule after electronic excitation. The LUMO  $\rightarrow$  HOMO transitions predicted by TD-DFT calculations were not observed experimentally in the fluorescence measurements due to the limited detection range of the fluorescence spectrophotometer employed. Instead, the

fluorescence spectra of **6a** and **6b** only show the emission bands due to the LUMO  $\rightarrow$  HOMO-1 transition, and their relatively weak intensity can be attributed to the mismatch of LUMO and HOMO-1 in spatial distribution (see Figure 3).

#### Redox Activities and FeCl<sub>3</sub>-induced Polymerization

The electrochemical redox properties of compounds 4a/b and 6a/b were investigated by cyclic voltammetric (CV) analysis. Figure 4 shows the cyclovotammograms of these compounds measured in dichloromethane at room temperature. For all of these compounds, no meaningful CV profiles could be determined in the window of the positive applied voltage, indicating that their electron-donating abilities are weak or poor. Such results are in line with their relatively low-lying HOMO energies in the ground state (S<sub>0</sub>) as disclosed by the DFT calculations (see Figure 5). When scanned within the window of negative voltage, the CV profiles of 4a/b and 6a/b show varied redox activities. For 6a, a weak cathodic peak is discernible at -0.73 V and in the reverse scan an anodic peak at -1.13 V is observed (Figure 4C). Overall, the voltammogram of **6a** features a highly irreversible redox pattern, and a significant reduction process can be seen in the forward CV scan with an onset at -1.18 V. In theory, the onset reduction potential can be correlated to the LUMO energy of the





**Figure 4.** Cyclic voltammograms of bithiophene derivatives **4a/b** and **6a/b** measured in  $CH_2CI_2$  in the presence of  $Bu_4NBF_4$  (0.1 M) as electrolyte at room temperature. Experimental conditions: working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: Ag/AgCI; scan rate: 0.1 V s<sup>-1</sup>.



Figure 5. Contours (isovalue = 0.032) and energies of the FMOs for ground singlet states ( $S_0$ ) of 4 a/b and 6 a/b calculated at the M06-2X/6-31G(d)//B3LYP/6-311 + G(d,p) levels.





molecule.<sup>[33a-c]</sup> In the voltammogram of **6b** (Figure 4D), a weak cathodic peak similar to that of **6a** is seen at -0.76 V. Following this anodic peak, a second anodic peak appears at -1.47 V, which is more prominent than the previous one and can be assigned to the reduction of **6b** by injection of an electron to its LUMO. The onset potential of this reduction process is at -1.20 V, which is slightly lower than that of **6a**. This experimental result is consistent with the DFT calculations which show the LUMO energies of 6a and 6b to be guite similar (Figure 5). Associated with the second cathodic peak is an anodic peak at -1.08 V in the voltammogram of **6b**, and the two of them form a quasi-reversible redox wave pair. There is another very weak anodic peak at -0.62 V detected in the reverse CV scan, which can be tentatively linked to the first cathodic peak as a redox couple. Comparatively, the CV data of 6a and 6b suggest that the thiophene-2-carbonyl group is more redox active and acts as a better electron-acceptor than the benzoyl group. The CV profiles of compounds 4a/b show similar guasi-reversible patterns (see Figure 4C and 4D). Compared with 6a/b, compounds 4a/b are more planar in structure and hence have much lower-lying LUMO energies as shown by the DFT calculations (Figure 5). In the CV profiles of 4 a/b, the onsets of reduction peaks are much lower than those of **6a/b**, corroborating the analysis based on DFT calculations.

There are many reports in which thiophenes have been used as building blocks for constructing  $\pi$ -conjugated polymers through oxidative polymerization.<sup>[2,34a-f]</sup> In order to investigate the newly synthesized thiophenes **4a/b** and **6a/b** for their potential for new organic optoelectronic materials, oxidative polymerization reactions of these compounds were conducted in chloroform using anhydrous FeCl<sub>3</sub> as oxidant (see Scheme 2). Under these conditions, **6a**, **4a** and **4b** furnished



Scheme 2. FeCl<sub>3</sub>-induced oxidative polymerization of thiophene derivatives 4a and 6a/b.

oligomers or polymers **7**, **8** and **9**, respectively. Polymerization of **6b** did not occur, as evidenced by the similarity in the UV-Vis absorption patterns of **6a** and the isolated product after treatment with FeCl<sub>3</sub>. The exact structures of polymers **7–9** have not been clearly identified at this juncture. Nevertheless, MALDI-TOF MS analysis suggests that they are mixtures of short oligomers mainly ranging from trimers to pentamers. Polymers **7–9** show relatively low solubility in common organic solvents, which hampers the characterization of their electrochemical properties in the solution phase. UV-Vis absorption and fluorescence spectroscopic analyses were successfully carried out on their chloroform solutions however and the detailed results are illustrated in Figure 6.



**Figure 6.** (A) Normalized UV-Vis absorption spectra of polymers **7–9** measured in CHCl<sub>3</sub> at room temperature. (B) Fluorescence spectra of polymers **7–9** measured in chloroform at room temperature. Excitation wavelengths ( $\lambda_{ex}$ ): **7** (392 nm), **8** (455 nm), and **9** (400 nm). Inset: photographic images of CHCl<sub>3</sub> solutions of **7–9** under irradiation of a UV lamp (254 nm).

As shown in Figure 6A, polymer 7 gives two distinctive  $\pi \rightarrow \pi^*$  absorption bands at 390 nm and 303 nm, which are of nearly equal intensity. Compared with the UV-Vis spectrum of 6a, the low-energy band of 7 is red-shifted by 12 nm, suggesting a moderate-to-low degree of increase in linear  $\pi$ -conjugation in the backbone of polymer 7. Scheme 2 shows a possible molecular structure of polymer 7, in which the polymerization occurs through the two terminal thienyl groups





in **6a** which are in cross-conjugation instead of linear conjugation. This is in line with the experimentally observed UV-Vis properties of 7. The UV-Vis absorption spectrum of polymer 8 features a strong band at 453 nm, which is considerably red-shifted relative to the low-energy absorption of its precursor 4a (312 nm). In the structure of 4a, the most reactive sites for oxidative polymerization are on the  $\pi$ conjugated bithienyl unit. Thus, oxidative polymerization of 4a could produce an oligothiophene backbone with a relatively high degree of linear  $\pi$ -conjugation as proposed in Scheme 2. In the spectrum of polymer 9, there are two weak and broad absorption shoulder bands discernible at 440 nm and 370 nm in the low-energy region. Compared with the UV-Vis spectrum of **6b**, polymer **9** does gain increased  $\pi$ -conjugation which results in significantly red-shifted low-energy absorptions. Nevertheless, the relative intensity of the low-energy bands in polymer 9 is a bit low. Given that there are three reactive thienyl moieties in the structure of **6b**, the polymerization very likely yields hyperbranched  $\pi$ -frameworks rather than linear polymers. Polymers 7-9 show much stronger fluorescence emissions than their precursors 6a and 4a/b; in particular, polymer 8 was observed to emit bright yellowish light upon UV irradiation (see the inset of Figure 6B). To further elucidate their emission properties, fluorescence spectra of 7-9 were measured in chloroform at room temperature and the detailed results are shown in Figure 6B. Of these polymers, polymer 8 shows the strongest fluorescence with a maximum emission wavelength ( $\lambda_{em}$ ) at 561 nm. The emission spectrum of polymer 7 shows a broad band peaking at 535 nm. Polymer 9 shows the weakest emission in comparison with the other polymers, but its  $\lambda_{em}$  (at 564 nm) is close to that of polymer **8**, suggesting a similar degree of  $\pi$ -conjugation between these two polymers. Overall, polymer 8 turns out to be the best fluorophore among these polymers, and it could potentially be used in the fields of organic fluorescent sensors and/or light-emitting devices.[35a-h] The fluorescence performance of 8 is attributed to its linearly and highly extended  $\pi$ -conjugated oligothiophene backbone. Further studies on the structure-fluorescence property relationships for these thiophene-based polymers are currently being undertaken.

## Conclusions

In conclusion, we have synthesized and studied the optoelectronic and redox properties of an initial series of new arylsubstituted bithiophene derivatives via a convenient procedure, not requiring expensive TM-catalysts, and related polymers. Their electronic absorption and emission properties were determined experimentally by UV-Vis and fluorescence spectroscopy in conjunction with TD-DFT computational analysis to gain deeper understanding on their structural, frontier molecular orbital, and vertical absorption/emission properties. Our studies have shown that terthiophene **6b** having quasireversible redox behaviour and the lowest band gap of 3.62 eV, may be a promising candidate to be further developed into a potentially useful small-molecule organic conductor or semiconductor. The band energy gaps for all four molecules reported herein are too high to be incorporated into new materials, since that their backbone geometries are not sufficiently rigid to be incorporated into useful  $\pi$ -conjugated materials.<sup>[2b]</sup> Terthiophene **4b** emits a blue light ( $\lambda_{em}$  = 390 nm) upon photoexcitation, while thiophene polymers **7** and **8** emit green and yellow fluorescent light respectively. Together, these new thiophene-based fluorophores can be potentially applied in the design and fabrication of organic light emitting devices. Further investigations of these compounds and other functionalized derivatives and their applications in materials science and technology are underway.

### **Supporting Information Summary**

Experimental details for the syntheses and spectral data of all new compounds reported herein are provided in the Supporting Information.

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# **Conflict of Interest**

The authors declare no conflict of interest.

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- G. Schopf; G. Koßmehl, Polythiophenes-Electrically Conductive Polymers, Springer, Berlin, Heidelberg, 1997.
- [2] a) J. Roncali, *Macromol. Rapid. Commun.* 2007, 28, 1763–1775; b) J. Roncali, *Chem. Rev.* 1992, 92, 711–738.
- [3] G. Barbarella, M. Melucci, G. Sotgiu, in Handbook of Thiophene-Based Materials: Applications in Organic Electronics and Photonics, eds. I. F. Perepichka ; D. F. Perepichka, John Wiley & Sons, 2009, vol. 17, pp. 1581–1593.
- [4] A. De Meijere, S. Bräse, M. Oestreich, Metal Catalyzed Cross-Coupling Reactions and More, John Wiley & Sons, 2013.
- [5] I. Osaka ; R. D. McCullough, Acc. Chem. Res. 2008, 41, 1202–1214.
- [6] B. J. Eckstein, F. S. Melkonyan, E. F. Manley, S. ;Fabiano, A. R. Mouat, L. X. Chen, A. Facchetti, T. J. Marks, . J. Am. Chem. Soc. 2017, 139, 14356–14359b) B. J. Eckstein, F. S. Melkonyan, N. Zhou, E. F. Manley, J. Smith, A. Timalsina, R. P. H. Chang, L. X. Chen, A. Facchetti, T. J. Marks, *Macromolecules* 2017, 50, 1430–1441c) F. S. Melkonyan, W. Zhao, M. Drees, N. D. Eastham, M. J. Leonardi, M. R. Butler, Z. Chen, X. Yu, R. P. H. Chang, M. A. Ratner, A.; Facchetti, T. J. Marks, *J. Am. Chem. Soc.* 2016, 138, 6944–6947.
- [7] a) A. Mishra, C.-Q. Ma, P. Bauerle, *Chem. Rev.* 2009, 109, 1141–1276.
  b) R. D. McCullough, *Adv. Mater.* 1998, 10, 93–116.
- [8] N. Somanathan, G. Wegner, Synth. Met. 1995, 75, 123–126.
- [9] M. R. Andersson, M. Berggren, G. Gustafsson, T. Hjertberg, O. Inganäs, O. Wennerström, Synth. Met. 1995, 71, 2183–2184.
- [10] G. Bidan, S. Guillerez ; V. Sorokin, Adv. Mater. 1996, 8, 157–160.





- [11] L. Robitaille, M. Leclerc, *Macromolecules* **1994**, *27*, 1847–1851.
- [12] E. L. Foster, C. Al Christopher, J. Mangadlao, R. Advincula, J. Mater. Chem. 2012, 22, 11025–11031.
- [13] R. Cagnoli, M. Lanzi, A. Mucci, F. Parenti, L. Schenetti, *Polymer* 2005, 46, 3588–3596.
- [14] M. A. Truong, S. Fukuta, T. Koganezawa, Y. Shoji, M. Ueda, T. Higashihara, J. Polym. Sci. Part A: Polym. Chem. 2015, 53, 875–887.
- [15] N. Hirota, N. Hisamatsu, S. Maeda, H. Tsukahara, K. Hyodo, Synth. Met. 1996, 80, 67–72.
- [16] M. I. Arroyo-Villan, G. A. Diaz-Quijada, M. S. Abdou, S. Holdcroft, *Macro-molecules* 1995, 28, 975–984.
- [17] C. D. Casa, P. C. Bizzarri, E. Salatelli, F. Bertinelli, Adv. Mater. 1995, 7, 1005–1009.
- [18] Y. Wei, C. C. Chan, J. Tian, G. W. Jang, K. F. Hsueh, Chem. Mater. 1991, 3, 888–897.
- [19] T. V. Richter, S. Link, R. Hanselmann, S. Ludwigs, Macromol. Rapid Commun. 2009, 30, 1323–1327.
- [20] M. Scheuble, M. Goll, S. Ludwigs, Macromol. Rapid Commun. 2015, 36, 115–137.
- [21] E. Zhou, Z. A. Tan, L. Huo, Y. He, C. Yang, Y. Li, J. Phys. Chem. B 2006, 110, 26062–26067.
- [22] M. Scheuble, T. V. Richter, M. Goll, S. Link, J. T. L. Navarrete, A. Ruff, M. C. R. Delgado, S. Ludwigs, *Polym. Chem.* 2014, *5*, 6824–6833.
- [23] G. Zotti, R. Salmaso, M. Gallazzi, R. Marin, Chem. Mater. 1997, 9, 791–795.
- [24] H. S. Mangold, T. V. Richter, S. Link, U. Würfel, S. Ludwigs, J. Phys. Chem. B 2011, 116, 154–159.
- [25] S. Himmelberger, D. T. Duong, J. E. Northrup, J. Rivnay, F. P. Koch, B. S. Beckingham, N. Stingelin, R. A. Segalman, S. C. Mannsfeld, A. Salleo, *Adv. Func. Mater.* 2015, *25*, 2616–2624.
- [26] a) G. Yin, Z. Wang, A. Chen, M. Gao, A. Wu, Y. Pan, J. Org. Chem. 2008, 73, 3377–3383; b) S. Khaghaninejad, M. M. Heravi, in Advances in Heterocyclic Chemistry, Elsevier, 2014, vol. 111, pp. 95–146; c) E. Campaigne, W. O. Foye, J. Org. Chem. 1952, 17, 1405–1412.
- [27] a) K. Gewald, Angew. Chem. 1961, 73, 114; b) For a more recent green approach see R. Chithiravel, K. Rajaguru, S. Muthusubramanian, N. Bhuvanesh RSC Adv. 2015, 5, 86414–86420.
- [28] a) H. Fiesselmann, G. Pfeiffer, Chem. Ber. 1954, 87, 848–856. b) W. You, X. Yan, Q. Liao, C. Xi, Org. Lett. 2010, 12, 3930–3933; c) A. Acharya, S. Vijay Kumar, B. Saraiah, H. Ila, J. Org. Chem. 2015, 80, 2884–2892; d) V. Guilarte, M. A. Fernández-Rodríguez, P. García-García, E. Hernando, R. Sanz, Org. Lett. 2011, 13, 5100–5103 e) H. Jiang, W. Zeng, Y. Li, W. Wu, L. Huang, W. Fu, J. Org. Chem. 2012, 77, 5179–5183; f) B. Gabriele, R. Mancuso, L. Veltri, V. Maltese ; G. Salerno, J. Org. Chem. 2012, 77, 9905–

9909; g) R. Mancuso, A. Maner, L. Cicco, F. M. Perna, V. Capriati, B. Gabriele, *Tetrahedron* 2016, *72*, 4239–4244; h) H. S. Lee, S. H. Kim ; J. N. Kim, *Tetrahedron Lett.* 2009, *50*, 6480–6483; i) C. R. Reddy, R. R. Valleti, M. D. Reddy, *J. Org. Chem.* 2013, *78*, 6495–6502; j) A. Acharya, G. Parameshwarappa, B. Saraiah, H. Ila, *J. Org. Chem.* 2014, *80*, 414–427; k) X. Luo, L.-S. Ge, X.-L. An, J.-H. Jin, Y. Wang, P.-P. Sun, W.-P. Deng, *J. Org. Chem.* 2015, *80*, 4611–4617; l) G. Saini, N. T. Lucas, J. Jacob, *Tetrahedron Lett.* 2010, *51*, 2965–2985.

- [29] T. R. Swaroop, R. Roopashree, H. Ila ; K. S. Rangappa, *Tetrahedron Lett.* 2013, 54, 147–150.
- [30] a) R. Cano, J. M. Perez, D. J. Ramon, G. P. McGlacken *Tetrahedron* 2016, 72, 1043–1050. b) S. Varello, S. T. Handy *Synthesis* 2009, 1, 138–142. c) T. Sone, K. Sato, U. Kazuaki, Y. Umetsu, A Yoshino, K. Takahashi, *Bull. Chem. Soc. Jpn.* 1994, *67*, 2187–2194.
- [31] Y. Zhao, D. G. Truhlar, Theor. Chem. Acc. 2008, 120, 215-241.
- [32] P. Stephens, F. Devlin, C. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623–11627.
- [33] a) A. MacColl, *Nature* 1949, *163*, 178–179. b) C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, G. C. Bazan, *Adv. Mater.* 2011, *23*, 2367–2371. c) Y. Yang, F. Arias, L. Echegoyen, L. F. Chibante, S. Flanagan, A. Robertson, L. J. Wilson, *J. Am. Chem. Soc.* 1995, *117*, 7801–7804.
- [34] a) G. Li, G. Koßmehl, H. P. Welzel, G. Engelmann, W. D. Hunnius, W. Plieth, H. Zhu, *Macromol. Chem. Phys.* **1998**, *199*, 525–533; b) P. Englebienne, M. Weiland, *Chem. Commun.* **1996**, 1651–1652; c) M. Chayer, K. Faid, M. Leclerc, *Chem. Mater.* **1997**, *9*, 2902–2905; d) D. larossi, A. Mucci, L. Schenetti, R. Seeber, F. Goldoni, M. Affronte, F. Nava, *Macromolecules* **1999**, *32*, 1390–1397; e) M. Fujitsuka, T. Sato, H. Segawa, T. Shimidzu, *Synth. Met.* **1995**, *69*, 309–310; f) T. Iyoda, M. Kitano, T. Shimidzu, *J. Chem. Soc., Chem. Commun.* **1991**, 1618–1619.
- [35] a) C. Li, M. Numata, M. Takeuchi, S. Shinkai, Angew. Chem. Inter. Ed. 2005, 44, 6371–6374; b) S. W. Thomas, G. D. Joly, T. M. Swager, Chem. Rev. 2007, 107, 1339–1386; c) M. Leclerc, Adv. Mater. 1999, 11, 1491–1498. d) Y. Tang, F. He, M. Yu, F. Feng, L. An, H. Sun, S. Wang, Y. Li, D. Zhu, Macromol. Rapid Commun. 2006, 27, 389–392; e) Wang, Q. Zhang, Z. De Liu, C. Z. Huang, Analyst 2012, 137, 5565–5570; f) P. Dyreklev, M. Berggren, O. Inganäs, M. R. Andersson, O. Wennerström, T. Hjertberg, Adv. Mater. 1995, 7, 43–45; g) I. F. Perepichka, D. F. Perepichka, H. Meng, F. Wudl, Adv. Mater. 2005, 17, 22G. Schopf ; G. Koßmehl, Polythiophenes-Electrically Conductive Polymers, Springer, Berlin, Heidelberg, 1997.

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