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Reactive Conducting Thiepin Polymers

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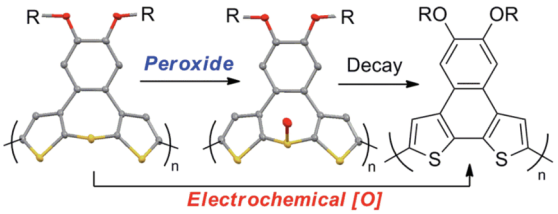
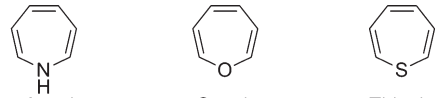


We report the design and synthesis of annulated thiepins designed to undergo bent-to-planar transformation driven by aromatization under electrochemical control. Thiepins are conjugated seven-membered ring systems with a thioether in the macrocycle. We synthesized thermally stable thiepins that are electropolymerizable to give rise to thiepin-containing electroactive polymers. Extended thiepin systems undergo sulfur extrusion with oxidation, and this feature has utility in peroxide sensing.

Introduction

We have had a long-standing interest in the design of polymers that undergo large conformational changes in response to an electrochemical stimulus for molecular actuators and other mechanically responsive applications.[1] A powerful driving force for such a conformational change is the aromatization (4n ± 2 π-electrons) energy gained from changes in the electronic configuration (oxidation or reduction) of molecules with 4n π-electrons, which initially prefer a bent geometry due to antiaromatic destabilization. Cyclooctatetraene- and thianthrene-based building blocks have been proposed for this purpose.[2] We have become interested in conjugated seven-membered ring systems that have a heteroatom with a lone pair of electrons: heteroepines (Chart 1). With the lone pair electrons on the heteroatoms heteroepines can be considered to be 8π-electron heteroannulenes, which are antiaromatic according to Hückel's rule. Thus, heteroepines are candidates for molecular actuators that can undergo "bent-to-planar" transformations under redox control. In this paper, we describe our efforts in the design of electroactive and reactive thiepin materials.

CHART 1. Heteroepins



Results and Discussion

Thermal Stability of Thiepins and Design of the Molecular Scaffold. The chemistries of azepine and oxepin are well documented,[3] but thiepin chemistry is relatively rare due to thermal instability of the parent molecule.[4] Compared to azepine and oxepin, thiepin is notoriously unstable and the parent molecule (without any substituents) has not been detected so far. It easily loses the sulfur atom and furnishes a benzenoid product. Sulfur extrusion is believed to occur by valence isomerization to the corresponding thianorcaradiene, followed by the cheletropic loss of sulfur (Scheme 1).[4,5] The pronounced instability is the result of the low activation energy of the sulfur extrusion step.

(1) (a) Baughman, R. *Synth. Met.* **1996**, *78*, 339–353. (b) Yu, H.-h.; Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, *125*, 1142–1143. (c) Song, C.; Swager, T. M. *Org. Lett.* **2008**, *10*, 3575–3578.

(2) (a) Marsella, M. J. *Acc. Chem. Res.* **2002**, *35*, 944–951. (b) Yu, H. -h.; Swager, T. M. *IEEE J. Oceanic Eng.* **2004**, *29*, 692–695.

(3) (a) Vogel, E.; Günther, H. *Angew. Chem., Int. Ed.* **1967**, *6*, 385–401. (b) Dewar, M. J. S.; Trinajstic, N. *Tetrahedron* **1970**, *26*, 4269–4267. (c) Paquette, L. A. *Angew. Chem., Int. Ed.* **1971**, *10*, 11–20.

(4) Murata, I.; Nakasuji, K. *Top. Curr. Chem.* **1981**, *97*, 33–70.

(5) Gleiter, R.; Krennrich, G.; Cremer, D.; Yamamoto, K.; Murata, I. *J. Am. Chem. Soc.* **1985**, *107*, 6874–6879.

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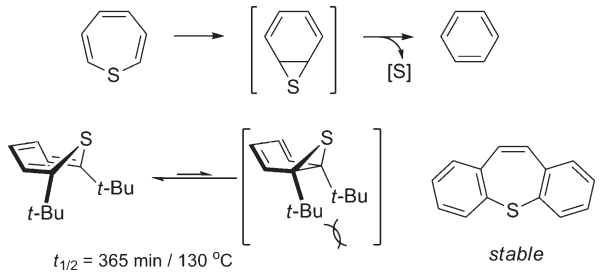
SCHEME 1. Sulfur Extrusion of Thiepin and Its Stabilization by Bulky Side Groups



Stable thiepins have been prepared by the addition of annulation and steric effects (Scheme 1). When bulky groups are introduced at the 2- and 7-positions, steric repulsion disfavors the thianorcaradiene intermediate and the molecules are thermally stable. If aromatic rings are annulated to thiepin, a substantial resonance energy loss accompanies valence-isomerization.[4]

Our design of the thiepin actuating molecular building block makes use of a stabilized annulated system containing two thiophenes and one benzene ring (Figure 1a). We chose thiophene annulation due to its electrochemical stability and ease of synthetic modification through the α-position of the annulated thiophenes (C3 and C10). Solubilizing groups could also be easily attached to the benzene moiety.

We calculated the optimal geometry (B3LYP, 3-21G) of the simple dithieno[*b*,*f*]benzo[*d*]thiepin (Figure 1b). As expected, the molecule of the neutral state adopts a bent geometry. The distance between the outmost carbons (from C3 to C10) is ~6.8 Å. The optimized geometry of the doubly oxidized molecule is nearly planar presumably due to the energy gain from its aromatic electronic structure. The distance between the outmost carbons in the planar conformation enlarges to ~7.6 Å, which is an 11% increase from the neutral state. It should be noted, however, that the geometry calculations (DFT) here have been conducted on molecules in a gas phase, which therefore may produce a certain discrepancy when the molecules are in a different environment (in solution/solid amorphous state, for example).

Synthesis of Thiophene-Annulated Thiepins. Yasuike et al. reported the synthesis of dithieno[*b*,*f*]thiepins via dilithium intermediates but did not investigate any applications.[6] Traditionally, annulated thiepins have been prepared by condensation, elimination, ring expansion or rearrangement, etc.[4] However, Yasuike's approach is modular, and they were able to prepare dithienoheteroepins containing group 14, 15, and 16 elements, including thiepins. This "dilithio" method has been applied to the preparation of

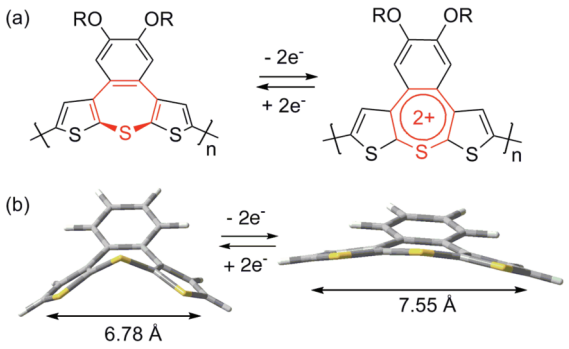


FIGURE 1. (a) Design of an annulated thiepin polymer. (b) Geometry-optimized (B3LYP, 3-21 g) structures of an annulated thiepin in its neutral (left) and doubly oxidized (right) states.

other heteroepins,[7] annulated thiophenes,[8] and various aromatic thioethers.[9] The typical source of sulfur is sulfur dichloride or bis(phenylsulfonyl) sulfide ($(PhSO_2)_2S$). However, the drawback is the generally low yields, typically ~30% for cyclic products.

We first followed the same "dilithio" method starting with bis(bromothienyl)benzene derivatives **2a**−**c**, which were prepared by selective NBS bromination of compounds **1a**−**c** (Scheme 2). Compounds **1a**−**c** were synthesized starting from catechol according to known procedures.[10] The dibromides **2a**−**c** were subjected to lithiation followed by substitution with sulfur sources. We were able to isolate the desired thiepin products **3a**−**c**, but the yields were less than 30%. Attempts to improve the yield by varying the solvent or temperature were not successful.

After noticing that sulfur dichloride could be a good electrophile in the aromatic electrophilic substitution, we tried a direct cyclization with compounds **1a**−**c**. This route was inspired by the preparation of 3,3′-dipyrrolyl sulfides using sulfur dichloride starting from substituted pyrroles.[11] In addition, the 2-position of thiophene is highly selective over 5-position in other electrophilic reactions (e.g., bromination). Fortunately, via the direct cyclization we were able to obtain the desired thiepins in good yields. It should be noted that sulfur dichloride needs to be freshly distilled just prior to use because it tends to decompose relatively quickly to sulfur monochloride (S_2Cl_2) and chlorine.

Thiepins **3a**−**c** are pale yellow and are crystalline powders even with the racemic 2-ethylhexyloxy side chains. The X-ray crystal structure of the methoxy derivative **3c** (Scheme 2) clearly shows the bent geometry at its neutral state. The distance between the outmost carbons (6.85 Å) is in good agreement with the value from the DFT calculation.

In order to examine the effect of the substitution pattern, we synthesized dithieno[3,2-*b*;2′,3′-*f*]benzo[*d*]thiepin **7**, which is isomeric to **3b** (Scheme 3). To incorporate bromines into the 3- and 3′-positions, **4** was first tetrabrominated and then subjected to debromination to compound **6**. This route was necessary because bromination occurs at the 5-positions first, and moreover, lithium−bromine exchange also favors the less sterically hindered 5-positions. Following the standard

(6) Yasuike, S.; Nakashima, F.; Kurita, J.; Tsuchiya, T. *Heterocycles* **1997**, *45*, 1899–1902.
(7) (a) Yasuike, S.; Ohta, H.; Shiratori, S.; Kurita, J.; Tsuchiya, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1817–1819. (b) Yasuike, S.; Shiratori, S.-i.; Kurita, J.; Tsuchiya, T. *Chem. Pharm. Bull.* **1999**, *47*, 1108–1114. (c) Yasuike, S.; Kiharada, T.; Tsuchiya, T.; Kurita, J. *Chem. Pharm. Bull.* **2003**, *51*, 1283–1288.
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(9) (a) Nakayama, J.; Katano, N.; Shimura, Y.; Sugihara, Y.; Ishii, A. *J. Org. Chem.* **1996**, *61*, 7608–7610. (b) Chahma, M.; Hicks, R. G.; Myles, D. J. T. *Macromolecules* **2004**, *37*, 2010–2012. (c) Chahma, M.; Myles, D. J. T.; Hicks, R. G. *Chem. Mater.* **2005**, *17*, 2672–2678.
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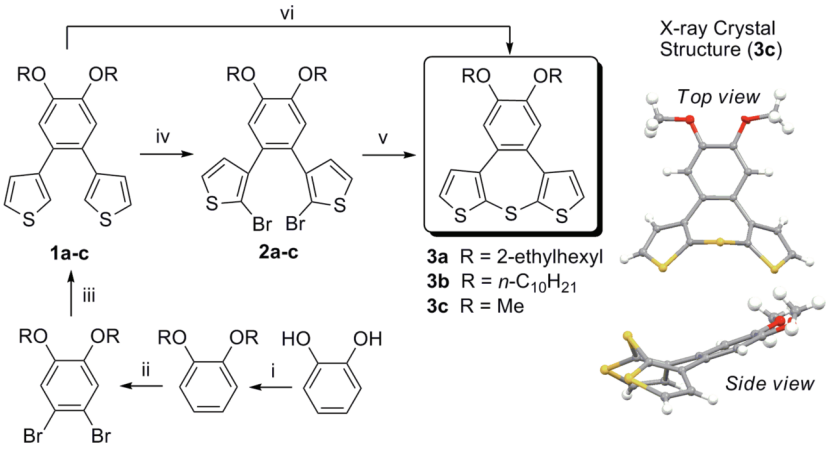
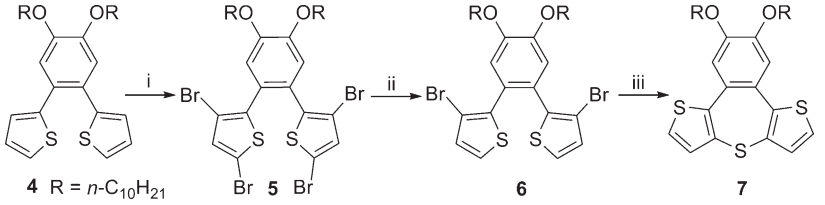
(11) Chen, Q.; Dolphin, D. *Synthesis* **2001**, 40–42.

SCHEME 2. Synthesis of Annulated Thiepins[a]



[a]Reagents: (i) K_2CO_3, 1-bromodecane, acetone, reflux, 1 d, 93%; (ii) Br_2, CH_2Cl_2, room temperature, 2 h, 96%; (iii) 3-thiophene boronic acid, Na_2CO_3, $Pd(PPh_3)_4$, toluene, EtOH, H_2O, reflux, 18 h, 94%; (iv) NBS, $CHCl_3$, acetic acid, room temperature, 89%; (v) *t*-BuLi, Et_2O or THF, then $(PhSO_2)_2S$ or SCl_2, −78 °C → room temperature, < 30%; (vi) SCl_2, CH_2Cl_2, −40 °C, 80%.

SCHEME 3. Synthesis of Isomeric Annulated Thiepin 7[a]



[a]Reagents: (i) NBS (4 equiv), $CHCl_3$, acetic acid, room temperature, 97%; (ii) *n*-BuLi, THF, −78 °C, 30 min, then MeOH, 90%; (iii) *t*-BuLi, Et_2O, $(PhSO_2)_2S$, −78 °C → room temperature, 15 h, 31%.

"dilithio" procedure we were able to obtain isomeric thiepin **7**, albeit in a low yield.

Cyclic Voltammograms of Annulated Thiepins. Figure 2 shows the cyclic voltammograms (CVs) of compounds **3c** and **7**. The CVs were taken in CH_2Cl_2 with 0.1 M $TBAPF_6$ as a supporting electrolyte on a Pt button electrode with a standard three-electrode configuration under ambient conditions.

Both CVs showed two 1-electron oxidation waves consistent with the oxidation of the thiepin π-systems from 8 to 6 π-electrons. Oxidation of **7** (0.73 V) occurred at a lower potential than **3c** (0.82 V vs Fc/Fc^+, the first half potentials). This difference can be rationalized by the positions where electrons or charges reside in the stable canonical resonance forms (Scheme 4). The radical in $\mathbf{7}^{\bullet+}$ can be benzylic and also in the favored α-position of the thiophene, while the benzylic radical in $\mathbf{3c}^{\bullet+}$ is at the β-position of the thiophenes.

The reduction waves of **3c** and **7** are quite different. The reduction from $\mathbf{3c}^{2+}$ to $\mathbf{3c}^{\bullet+}$ appears as a sharp peak, which is at a lower potential than expected. We attribute this to the aromatic energy gain after the second oxidation (8 to 6 π-electrons). In other words, the dication $\mathbf{3c}^{2+}$ is stabilized by planarization and a overpotential is required to rereduce the molecule. The reduction for $\mathbf{7}^{2+}$ was not complete at a normal potential range, but an additional reduction peak appeared at the very lower potential (~−0.5 V vs Fc/Fc^+). This type of reduction occurs only from the $\mathbf{7}^{2+}$, not from $\mathbf{7}^{\bullet+}$ as evidenced by reversing the scan after first oxidation (Figure 2b, blue dotted line). The charge trapping observed could be the result of some reversible intermolecular chemical bonding or a solid state (aggregation) effect.

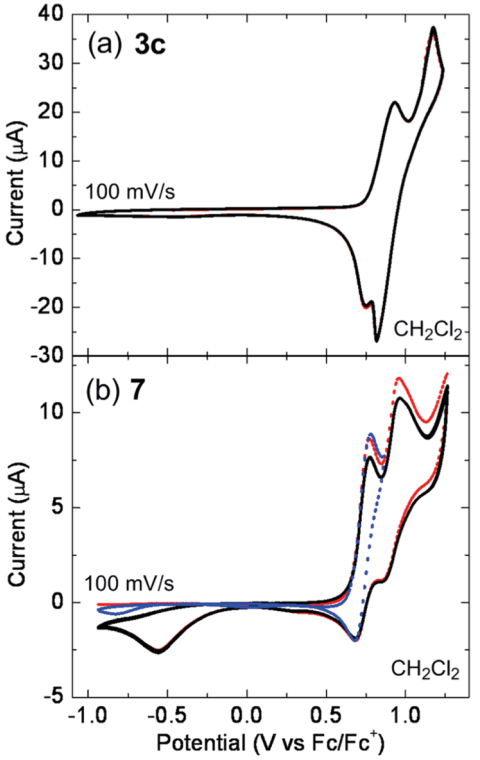
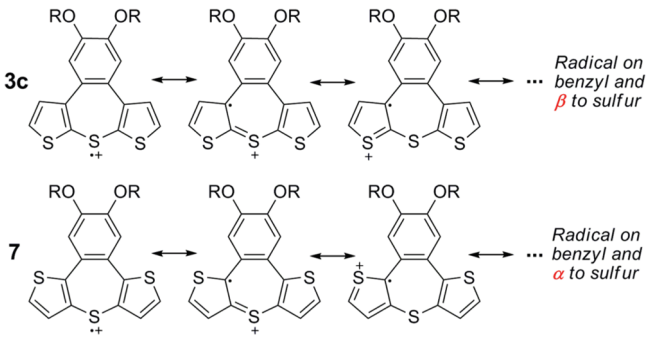


FIGURE 2. CVs of **3c** (a) and **7** (b) in CH_2Cl_2 with 0.1 M $TBAPF_6$ as a supporting electrolyte. The red dotted lines represent the first scans. The blue dotted line (b) shows the behavior when reversed after the first oxidation wave.

SCHEME 4. Proposed Charge Delocalization of Thiepin's Radical Cation

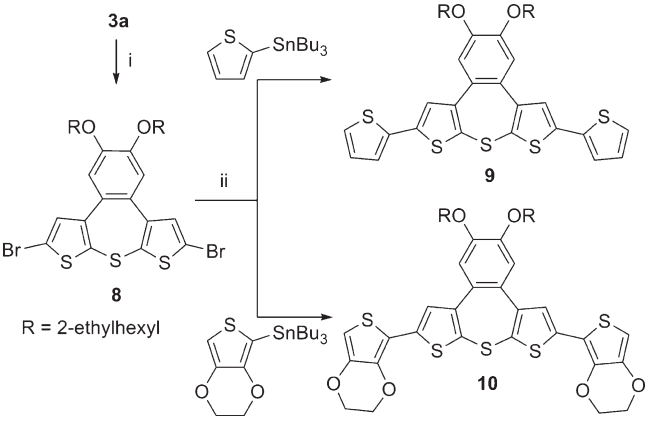


In short, both thiepin **3c** and **7** showed two 1-electron redox events, which are reproducible and chemically reversible under the above conditions. The annulation pattern influences the molecule's oxidation and reduction potentials. The sharp reduction from $\mathbf{3c}^{2+}$ to $\mathbf{3c}^{\bullet+}$ is consistent with our proposal of planarization by aromatic energy gain.

Electropolymerization of Extended Thiepins. We focused on the molecule **3**-types of thiepins ([2,3-*b*]-annulation), and synthesized electropolymerizable thiepins **9** and **10** by bromination of **3a**, followed by Stille coupling reactions (Scheme 5).

Electropolymerizations successfully yielded thin polymer films with monomer solutions in 1:1 mixture of CH_2Cl_2 and CH_3CN with 0.1 M $TBAPF_6$ as a supporting electrolyte

SCHEME 5. Synthesis of Electropolymerizable Thiepin Monomers[a]



[a]Reagents: (i) NBS, $CHCl_3$, acetic acid, room temperature, 76%; (ii) $PdCl_2(PPh_3)_2$, DMF, 80 °C, 15 h, 78−80%.

under swept potential conditions (Figure 3a). In pure CH_2Cl_2 solvent we obtained a polymer growth, but the resulting polymers were loosely bound to the electrodes and were washed away with any manipulation. Both monomers **9** and **10** displayed a linear growth in redox currents with each potential scan. Poly(**9**) and poly(**10**) displayed similar behaviors characteristic of conjugated polymers, and the electrochemical characterization of poly(**9**) is shown in Figure 3. Scan-rate dependence of thin films of poly(**9**) in

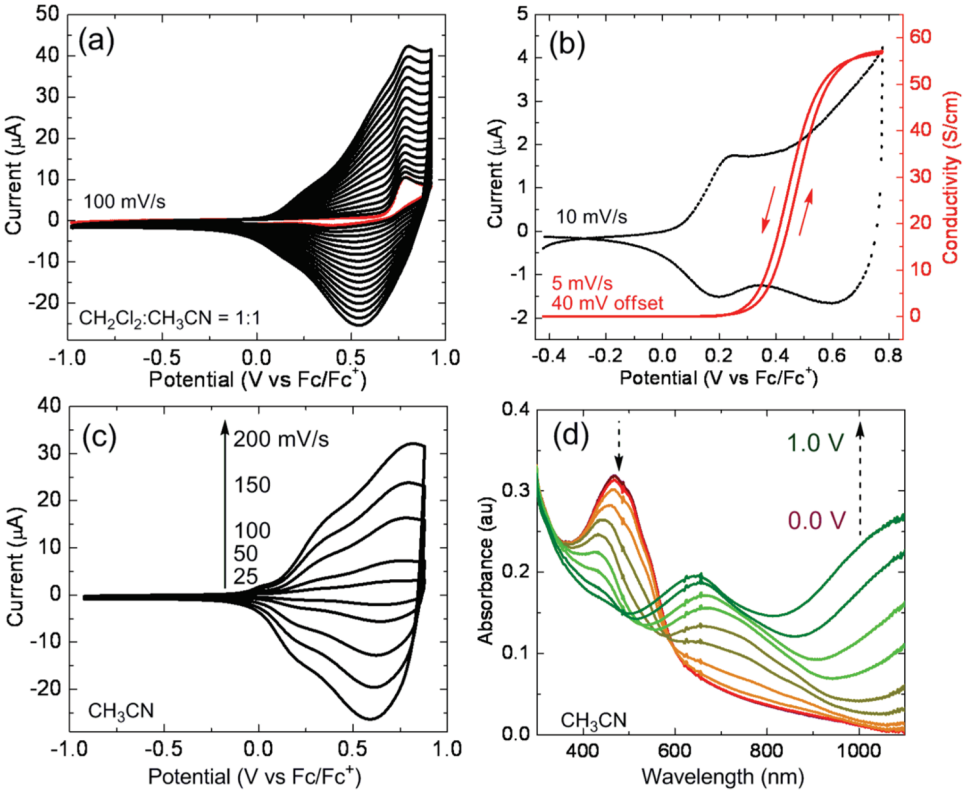
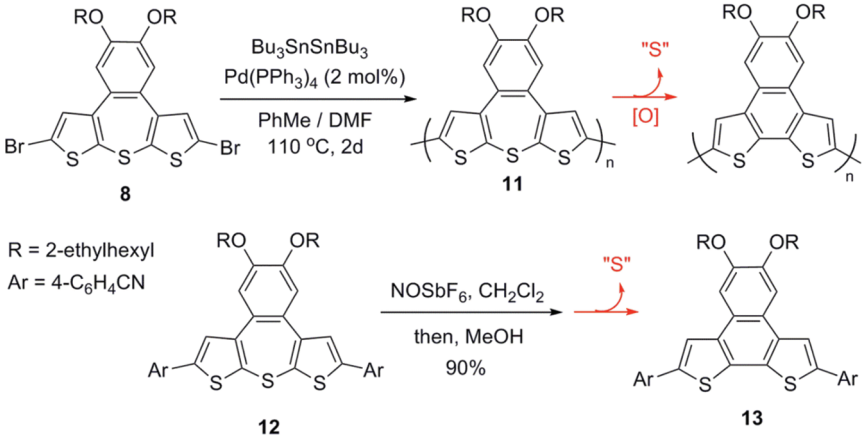


FIGURE 3. (a) Electropolymerization of **9** on a Pt button electrode in a 1:1 mixture of CH_2Cl_2 and CH_3CN. The red dotted line represents the first scan. (b) CV (dotted line) and in situ conductivity measurement (solid line) of the film of poly(**9**) on a 5 μm interdigitated Pt microelectrode in CH_3CN. (c) CVs of the film of poly(**9**) at different scan rates. (d) Electronic absorption spectra of the film of poly(**9**) on an ITO-coated glass electrode in CH_3CN as a function of oxidation potential from 0.0 to 1.0 V vs Ag/Ag^+. $TBAPF_6$ (0.1 M) was used as a supporting electrolyte in all cases.

SCHEME 6. Sulfur Extrusion of Thiepin Polymer 11 and Model Compound 12 upon Oxidation



the monomer-free solution (CH_3CN) is linear (Figure 3c), but as the films grow thicker the peak potentials shift at fast scan rates, suggesting limited ion diffusion. In situ conductivity measurements revealed the maximum conductivities were ~60−70 S/cm for both poly(**9**) and poly(**10**) (Figure 3b). Spectroelectrochemical measurements show very delocalized electronic structures, especially at high doping levels (Figure 3d).

Thin electrochemically deposited films are not always easily characterized. However, we noticed in the CVs that the redox couple at the low potentials, ~0.2 V for poly(**9**) and ~−0.1 V for poly(**10**) (all vs Fc/Fc^+), and the overall electrochemical behavior was very similar to poly(dithienonaphthalene)s, which were reported previously in our group by using a tandem cyclization and polymerization mechanism.[10,12] The molecular structure of dithienonaphthalene is identical to the structure obtained if the sulfur is extruded in the thiepins. Moreover, after repeated redox cycling vibrational fine structure became more evident in the absorption of poly(**10**) in its neutral state, which is unusual for this type of (flexible) polymer. The above observations imply that the polymers have changed to rigid molecular frames, presumably due to the sulfur extrusion in the polymers.

Our sulfur extrusion hypothesis with oxidation was confirmed with thiepin polymers prepared via cross-coupling chemistry and model compounds (Scheme 6). Specifically when we measured the electroactivity of the drop-cast films of chemically synthesized thiepin polymers (Figure 4) the onset of the first scan (~0.9 V) shifted irreversibly to lower potentials (~0.3 V, all vs Fc/Fc^+) with oxidative redox cycling. Furthermore, upon reversing of the high potential in the first scan, the return current crosses the trace of the initial anodic potential sweep. This feature shows that we are creating a species that is more easily oxidized than the parent material and is suggestive of irreversible reactions. The profiles of successive scans resembled those of reported poly(dithienonaphthalene)s,[12] the structures that result after sulfur extrusion from the polymers.

We also observed sulfur extrusion in a substituted thiepin model compound with oxidation by nitrosonium ion. Bisaryl (4-cyanophenyl)-substituted thiepin compound **12** was prepared and subject to an oxidation, followed by a reduction by MeOH. We were able to obtain in a high yield the desufurized product **13**, which was confirmed by NMR and MS (Supporting Information). Thus, based on the above results, we conclude that oxidized thiophene-annulated thiepins are unstable and prone to sulfur extrusion. However, it should be noted here that as Figure 2 illustrates, thiophene-annulated thiepins are electrochemically stable when there is no substitution at 2,2′-positions.

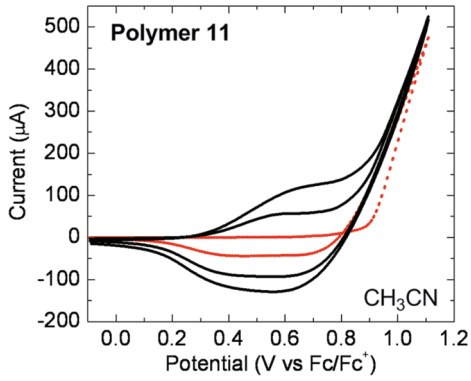


FIGURE 4. CVs of a drop-cast film of polymer **11** on an ITO-coated glass electrode in CH_3CN with 0.1 M $TBAPF_6$ as a supporting electrolyte. The dotted line represents the first scan.

Properties of Thiepin 1-Oxide (Sulfoxide). The fact that substituted annulated thiepins are labile when oxidized prevented the desired electrochemical utility. However, the sulfur extrusion from the annulated thiepins produces dithienonaphthalenes, which are very rigid, stable, and luminescent. As a result, we can expect a large optical signal change if we chemically affect this transition from the bent, flexible, and nondelocalized annulated thiepin. It is also known that thiepin 1-oxides (sulfoxide) are less thermally stable than thiepins,[13] and even sterically or electronically stabilized thiepin 1-oxides are easily converted to the benzenoid compounds, presumably through the same valence-isomerization sulfur-extrusion mechanism. It should be noted that unlike thiepin 1-oxides, thiepin 1,1-dioxides (sulfones) are known to be thermally very stable. In fact, the parent thiepin

(12) Tova, J. D.; Swager, T. M. *Adv. Mater.* **2001**, *13*, 1775–1780.

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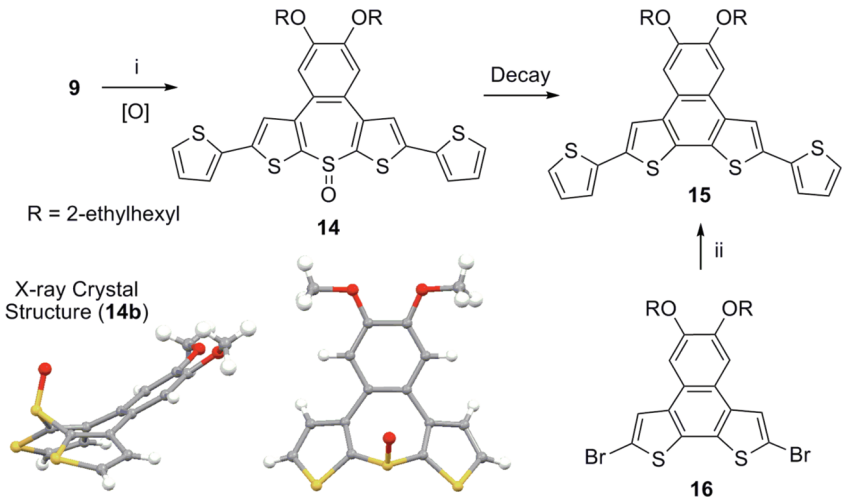
SCHEME 7. Synthesis of Thiepin Oxide 14 and Dithienonaphthalene 15[a]



[a]Reagents: (i) *m*-Chloroperoxybenzoic acid, CH_2Cl_2, −20 °C, 1 h, 55%; (ii) 2-tributylstannylthiophene, $PdCl_2(PPh_3)_2$, DMF, 80 °C, 15 h, 70%.

1,1-dioxide has been isolated as a stable compound at room temperature.[4,14]

Based upon our analysis, if an initially nonemissive or weakly emissive thiepin molecule encounters peroxides the thiepins can be converted to thiepin 1-oxide, which will transform rapidly into a highly fluorescent benzenoid compound. Organic peroxides have been used in explosives (e.g., tricycloacetone peroxides or TCAP), and their detection is of increasing importance. Thus, we decided to investigate the potential of the annulated thiepins as peroxide sensors.

We first synthesized the thiepin 1-oxide **14** from thiepin **9** by reaction with *m*-chloroperoxybenzoic acid in CH_2Cl_2 at low temperature (Scheme 7). With 1 equiv of peroxide, thiepin 1,1-dioxide was also formed as a byproduct in ~15% yield. We were able to isolate the thiepin 1-oxide **14** as a crystalline solid but it slowly decomposed at room temperature. However, it was stable enough to be characterized, and we obtained a single crystal of unsubstituted thiepin oxide **14b** at −20 °C (Scheme 7).

The molecular structure of thiepin 1-oxide **14b** is similar to that of thiepin **3c** with a slight increase in the distance between the outmost carbons (6.897 vs 6.853 Å). In the ^{1}H NMR spectrum there were two sets of signals in a roughly 3:1 ratio, indicating two isomers are present. The X-ray crystal structure shows the oxygen in the *endo*(axial)-position. However, thiepin 1-oxide with the oxygen in the *exo*(equatorial)-position is also present. An X-ray structure of a related benzothiepin 1-oxide with sulfoxide oxygen's *exo*-position was previously reported.[15] For comparison, dithienonaphthalene **15** was prepared by Stille coupling reaction with compound **16**, which was prepared by following the literature procedure.[10]

We examined the fluorescence changes when thiepin **9** was exposed to a peroxide. In a cuvette containing a CH_2Cl_2 solution of **9** we added one drop of a CH_2Cl_2 solution containing *m*-chloroperoxybenzoic acid (~0.05 M, excess) and monitored the increasing fluorescence intensity as time progressed (Figure 5). Initially, thiepin **9** displayed a weak

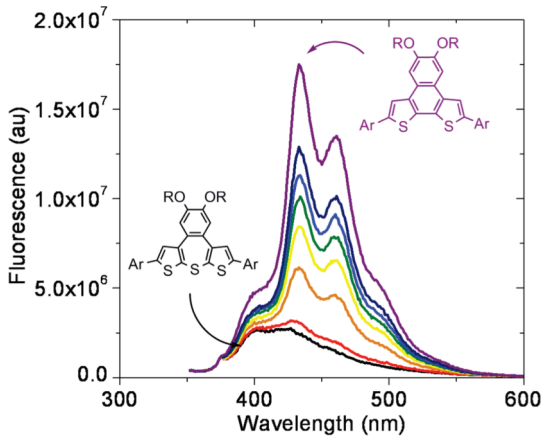


FIGURE 5. Time evolution (total 30 min) of emission spectra from the oxidation of **9** (Ar = 2-thienyl) in the presence of *m*-chloroperoxybenzoic acid (excess) at room temperature in CH_2Cl_2 to produce **15**. The excitation wavelength was 360 nm.

emission at around 400 nm. However, upon peroxide exposure, a relatively strong emission at 430 nm emerged, which matches dithienonaphthalene **15**'s fluorescence (Supporting Information). The fluorescence spectrum of the intermediate thiepin oxide **14** is similar to that of thiepin **9**; thus, the 430 nm fluorescence increased strictly as the result of the formation of **15**. This "turn-on" scheme can be utilized for a peroxide sensor.

Conclusion

We have designed and synthesized annulated thiepin systems which undergo bent-to-planar transformation driven by aromatization under electrochemical control. In the cyclic voltammetry, annulated thiepin (**3c**) showed a very interesting sharp peak at the reduction of its dication, suggestive of aromatic energy gains in the doubly oxidized thiepin. Extended thiepin systems, in spite of the thermal stability in the neutral state, were found to be unstable when oxidized, and sulfur extrusion is observed. Such a property is useful in peroxide sensing, and we exploited the fact that the

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(15) Hofmann, H.; Böhme, R.; Wilhelm, E. *Chem. Ber.* **1978**, *111*, 309.

sulfoxide has an even lower extrusion barrier than sulfur itself. The increased fluorescence originated from the extrusion products, which showed a potential as a "turn-on" sensor for peroxides.

Experimental Section

Materials. SCl_2 was synthesized from S_2Cl_2 with Cl_2 according to the literature method[16] and freshly distilled with a few drops of PCl_3 prior to use. Anhydrous DMF was purchased from Aldrich as Sure-Seal Bottles and used as received. THF, anhydrous CH_2Cl_2, and toluene were purified by passage through two alumina columns of an Innovative Technologies purification system. All other chemicals were of reagent grade and used as received.

6,7-Di(2-ethylhexyloxy)benzo[*d*]dithieno[2,3-*b*;3′,2′-*f*]thiepin (3a). Freshly distilled SCl_2 (2.1 mL, 16.5 mmol) in CH_2Cl_2 (100 mL) was added dropwise to a CH_2Cl_2 (450 mL) solution of compound **1a** (7.48 g, 15 mmol) at −40 °C under Ar. The mixture was slowly warmed to room temperature and stirred for 15 h, at which time the mixture was poured into 10% aqueous $NaHCO_3$. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude mixture was subjected to column chromatography (dichloromethane/hexane = 1:10). The product was further purified by recrystallization (dichloromethane/methanol). Yield: 6.04 g (76%) of lightly yellow solid. T_m = 87−89 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.25 (d, 2H, J = 5.5 Hz), 7.13 (d, 2H, J = 5.5 Hz), 7.05 (s, 2H), 3.96 (m, 4H), 1.82 (m, 2H), 1.57−1.34 (m, 16H), 0.94 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 148.9, 145.3, 130.7, 129.4, 128.0, 126.4, 114.1, 71.7, 39.8, 30.8, 29.3, 24.2, 23.3, 14.3, 11.4. HR-MS (ESI): calcd for $C_{30}H_{40}O_2S_3$ $[M + Na]^+$ 551.2083, found 551.2077.

6,7-Di(decyloxy)benzo[*d*]dithieno[3,2-*b*;2′,3′-*f*]thiepin (7). To a cooled (−78 °C) Et_2O (50 mL) solution of compound **6** (0.713 g, 1 mmol) was added dropwise *t*-BuLi (1.7 M in hexane, 2.41 mL, 4.1 mmol). The initially cloudy mixture became clear as lithiation proceeded. After the mixture was stirred at −78 °C for 10 min, $(PhSO_2)_2S$ was added in portions. The mixture was allowed to stir at −78 °C for 3 h and then at room temperature for another 12 h. After being diluted with diethyl ether, the mixture was washed with 10% aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude mixture was subjected to column chromatography (chloroform/hexane = 1:7). Yield: 0.181 g (31%) of light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (d, 2H, J = 5.2 Hz), 7.10 (s, 2H), 6.93 (d, 2H, J = 5.2 Hz), 4.09 (m, 4H), 1.87 (m, 4H), 1.50 (m, 4H), 1.40−1.28 (m, 24H), 0.89 (t, 6H, J = 6.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.2, 143.2, 131.5, 130.7, 125.9, 125.8, 115.4, 69.5, 32.1, 29.9, 29.8, 29.6, 29.6, 29.4, 26.2, 22.9, 14.4. HR-MS (ESI): calcd for $C_{34}H_{48}O_2S_3$ $[M + Na]^+$ 607.2709, found 607.2711.

6,7-Di(2-ethylhexyloxy)-3,10-bis(thiophene-2-yl)benzo[*d*]dithieno-[2,3-*b*;3′,2′-*f*]thiepin (9). To a degassed solution of DMF (5 mL) of compound **8** (0.350 g, 0.5 mmol) were added 2-tributylstannylthiophene (0.368 mL, 1.1 mmol) and $PdCl_2(PPh_3)_2$ (18 mg, 5 mol %). The mixture was allowed to stir at 80 °C for 15 h, at which time the mixture was cooled to room temperature. Ethyl aceate was added to the mixture, and the organic layer was washed with saturated aqueous NH_4Cl, KF, and NH_4Cl again. After being dried over $MgSO_4$, the organic layer was evaporated under reduced pressure and subjected to column chromatography (dichloromethane/hexane = 1:3). The product was further purified by recrystallization (dichloromethane/methanol). Yield: 0.270 g (78%) of pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (dd, 2H, J = 5.1, 1.0 Hz), 7.18 (s, 2H), 7.16 (dd, 2H, J = 3.6, 1.0 Hz), 7.10 (s, 2H), 7.12 (dd, 2H, J = 5.1, 3.6 Hz), 3.95 (m, 4H), 1.82 (m, 2H), 1.57−1.34 (m, 16H), 0.99−0.91 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.1, 146.0, 138.1, 136.9, 128.9, 128.1, 127.9, 125.7, 125.2, 124.5, 113.9, 71.8, 39.8, 30.8, 29.4, 24.2, 23.3, 14.3, 11.5. HR-MS (ESI): calcd for $C_{38}H_{44}O_2S_5$ $[M + Na]^+$ 715.1837, found 715.1869.

Polymer 11. Compound **8** (0.069 g, 0.1 mmol) and hexabutylditin (0.058 mL, 0.11 mmol) were dissolved in toluene (1.5 mL) and DMF (1.5 mL). The mixture was degassed with Ar for 40 min, and $Pd(PPh_3)_4$ (2.4 mg, 2 mol %) was added under gentle Ar stream. The mixture was allowed to stir at 110 °C for 2 d, at which time the mixture was cooled to room temperature and methanol was added to precipitate. The filtered solid was redissolved in $CHCl_3$ and added to acetone to precipitate again. The product was filtered and dried under air. Yield: 0.041 g (78%) of crimson solid. GPC (polystyrene standard): M_n = 6170, M_w = 7790, PDI = 1.26. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.15 (aromatic C-H), 7.03 (aromatic C-H), 3.95 (aliphatic C-H), 1.84−0.92 (aliphatic C-H).

6,7-Di(2-ethylhexyloxy)-3,10-bis(thiophene-2-yl)benzo[*d*]dithieno-[2,3-*b*;3′,2′-*f*]thiepin 1-Oxide (14). To a CH_2Cl_2 (1 mL) solution of **9** (0.029 g, 0.042 mmol) was added *m*-chloroperoxybenzoic acid (assumed as 72% purity, 0.010 g, 0.042 mmol) in CH_2Cl_2 (0.5 mL) at −20 °C, and the mixture was allowed to stir for 1 h. After being warmed to room temperature, the mixture was diluted with CH_2Cl_2, and washed with saturated $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (ethyl acetate/hexane/chloroform = 1:7:1). Yield: 0.015 g (51%) of pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) for *endo* (*axial*) δ: 7.47 (s, 2H), 7.33 (dd, 2H, J = 5.1, 1.0 Hz), 7.33 (s, 2H), 7.29 (dd, 2H, J = 3.6, 1.0 Hz), 7.08 (dd, 2H, J = 5.1, 3.6 Hz), 4.16 (m, 4H), 1.90 (m, 4H), 1.53−1.27 (m, 20H), 0.90 (t, 6H, J = 6.8 Hz). For *exo* (*equatorial*) δ: 7.28 (dd, 2H, J = 5.1, 1.0 Hz), 7.26 (s, 2H), 7.23 (dd, 2H, J = 3.6, 1.0 Hz), 7.10 (s, 2H), 7.05 (dd, 2H, J = 5.1, 3.6 Hz), 4.16 (m, 4H), 1.90 (m, 4H), 1.53−1.27 (m, 20H), 0.90 (t, 6H, J = 6.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) for *endo* (*axial*) δ: 149.4, 141.7, 139.3, 136.3, 135.7, 128.4, 127.1, 126.5, 125.9, 125.4, 114.0, 69.6, 32.0, 29.6, 29.5, 29.5, 26.3, 22.9, 14.3. For *exo* (*equatorial*) δ: 149.2, 139.7, 139.6, 135.2, 134.8, 128.3, 126.3, 125.9, 124.8, 118.8, 113.8, 69.6, 32.0, 29.6, 29.5, 29.5, 26.3, 22.9, 14.3. HR-MS (ESI): calcd for $C_{38}H_{44}O_3S_5$ $[M + H]^+$ 709.1967, found 709.1979.

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Supporting Information Available: Detailed experimental procedures for the synthesis of all other compounds. Crystallographic data for **3c** and **14b**. Cyclic voltammogram of the chemically synthesized thiepin polymer. Fluorescence spectrum of dithienonaphthalene **15**. ^{1}H and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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