

# Acetylenic Phenylthiafulvene: A Versatile Synthone for TTFV-Based Macromolecules

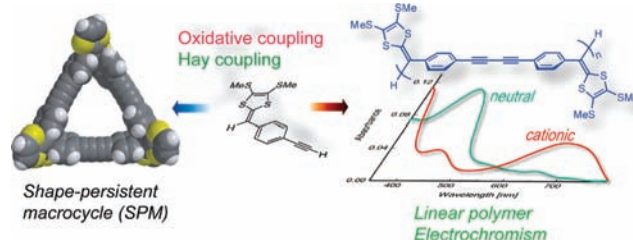
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## ABSTRACT



An acetylenic phenylthiafulvene was developed as a versatile synthone for diverse TTFV-based macromolecular scaffolds. Through different coupling reaction sequences, shape-persistent macrocycles and linear TTFV-embedded polymers have been obtained and thereafter characterized by spectroscopic and voltammetric analyses. The TTFV polymer thin films generated via electropolymerization of a dithiafulvenyl-end-capped diyne monomer showed promising prospects in electrochromic and redox switchable molecular devices.

Tetrathiafulvalene (TTF) and related analogues present an important class of electroactive building blocks extensively used in the development of functional organic electronic materials and devices.<sup>1</sup> Much attention in recent research of TTF has been devoted to the preparation of  $\pi$ -extended TTF (exTTF) derivatives, wherein diverse  $\pi$ -conjugated spacers are placed between the dithiole rings with the intention of modifying electronic characteristics, increasing dimensionality, and achieving multistage redox properties.<sup>1,2</sup> Among numerous TTF variants reported in the literature, exTTFs derived from insertion of a vinyl spacer in the TTF framework constitute an intriguing class of organic elec-

tronic materials, commonly referred to as TTF vinylologues (TTFVs).<sup>2b,3</sup> Like the simple TTF molecule, TTFVs can readily release two electrons to form stable dication upon oxidation, while the detailed electron transfer processes are usually associated with conformational changes that are substituent-dependent.<sup>3</sup>

Of great interest is the bistate conformational switching of diaryl-substituted TTFVs in response to different redox conditions. Previous crystallographic and theoretical studies<sup>3b,d,e,4</sup> have revealed that diphenyl-substituted TTFV

(1) For recent reviews, see: (a) Canevet, D.; Sallé, M.; Zhang, G.; Zhu, D. *Chem. Commun.* **2009**, 2245–2269. (b) *TTF Chemistry: Fundamental and Applications of Tetrathiafulvalene*; Yamada, J.-i., Sugimoto, T., Eds.; Springer-Verlag: Heidelberg, 2004. (c) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891–4946. (d) Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372–1409. (e) Nielsen, M. B.; Lomholt, C.; Becher, J. *Chem. Soc. Rev.* **2000**, *29*, 153–164. (f) Bryce, M. R. *Adv. Mater.* **1999**, *11*, 11–23. (g) Jørgensen, T.; Hansen, T. K.; Becher, J. *Chem. Soc. Rev.* **1994**, *23*, 41–51.

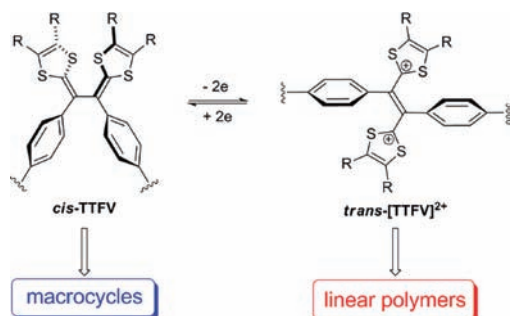
(2) (a) Adam, M.; Müllen, K. *Adv. Mater.* **1994**, *6*, 439–459. (b) Roncali, J. J. *Mater. Chem.* **1997**, *7*, 2307–2321.

(3) (a) Frère, P.; Skabara, P. J. *Chem. Soc. Rev.* **2005**, *34*, 69–98. (b) Guerro, M.; Carlier, R.; Boubekeur, K.; Lorcy, D.; Hapiot, P. *J. Am. Chem. Soc.* **2003**, *125*, 3159–3167. (c) Bellec, N.; Boubekeur, K.; Carlier, R.; Hapiot, P.; Lorcy, D.; Tallec, A. *J. Phys. Chem. A* **2000**, *104*, 9750–9759. (d) Hascoat, P.; Lorcy, D.; Robert, A.; Carlier, R.; Tallec, A.; Boubekeur, K.; Batail, P. *J. Org. Chem.* **1997**, *62*, 6086–6089. (e) Hapiot, P.; Lorcy, D.; Tallec, A.; Carlier, R.; Robert, A. *J. Phys. Chem.* **1996**, *100*, 14823–14827.

(4) (a) Yamashita, Y.; Tomura, M.; Tanaka, S.; Imaeda, K. *Synth. Met.* **1999**, *102*, 1730–1731. (b) Yamashita, Y.; Tomura, M.; Zaman, M. B.; Imaeda, K. *Chem. Commun.* **1998**, 1657–1658. (c) Tomura, M.; Yamashita, Y. *CrysEngComm* **2000**, *2*, 86–88. (d) Yamashita, Y.; Tomura, M.; Imaeda, K. *Tetrahedron Lett.* **2001**, *42*, 4191–4193.

derivatives tend to adopt a wedgelike structure in the neutral state, wherein the two dithiole rings are in a pseudo-*cisoid* orientation due to steric interactions. In contrast, the dications of such TTFVs prefer a pseudo-*transoid* conformation to minimize the disfavored electrostatic repulsion imposed by the dithiolium units (see Scheme 1). The switching property

**Scheme 1.** Conformational Switching of Diphenyl-Substituted TTFV in Response to Redox Conditions

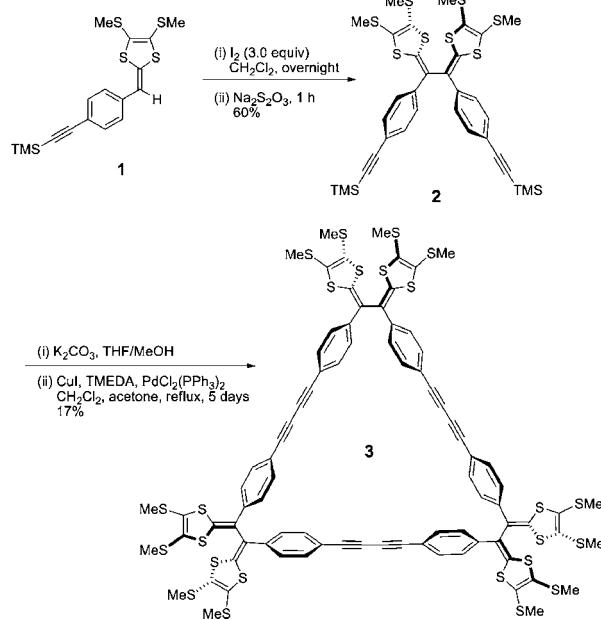


is useful in developing molecular devices (e.g., switches, motors, sensors, etc.); however, its ramifications in synthetic chemistry have been rarely explored.

In view of the conformational switching behavior shown in Scheme 1, it is conceivable that skeletal expansion based on the two isomeric building blocks (e.g., via oligo/polymerization reactions) would result in two distinct macromolecular consequences: the wedgelike neutral *cis*-TTFV would favor the assembly of shape-persistent macrocycles (SPMs) in a manner similar to that for numerous *m*-phenylene-based macrocyclophanes as demonstrated in the literature,<sup>5</sup> whereas the *trans*-[TTFV]<sup>2+</sup> should lead to the formation of linear oligomer/polymer chains.<sup>6</sup> To experimentally corroborate this hypothesis, an acetylenic phenyldithiafulvene synthon **1** (Scheme 2) was developed. The presence of acetylenic and dithiafulvenyl (DTF) units in compound **1** gives rise to dual reactivity for the construction of diverse  $\pi$ -conjugated frameworks. On the one hand, structural expansion can be readily achieved through acetylene coupling reactions (e.g., Heck, Sonogashira, and Hay). On the other hand, the DTF unit offers a facile synthetic handle to form TTFV-linked polymers via oxidative dimerization.

Scheme 2 outlines the synthesis of a triangular-shaped TTFV-phenylacetylene macrocycle **3** using acetylenic DTF **1** as the starting material. DTF **1** was obtained through a Horner–Wittig olefination reaction (see the Supporting Information). Upon oxidative coupling in the presence of molecular iodine, followed by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> reduction, DTF **1**

**Scheme 2.** Synthesis of TTFV-Based Macrocycle **3**



readily dimerized into TTFV **2** in 60% yield. Removal of the trimethylsilyl (TMS) groups of **2** with K<sub>2</sub>CO<sub>3</sub> in THF/MeOH yielded a terminal alkyne, which was immediately subjected to an intermolecular macrocyclization reaction to afford macrocycle **3** under dilute conditions (ca. 2.8 mM). This macrocyclization involved 3-fold Hay couplings,<sup>7</sup> while a satisfactory yield of 17% was attained under the catalysis of CuI/TMEDA and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.<sup>8</sup> Macrocycle **3** is a stable yellow solid that was readily purified through flash column chromatography. The byproducts of this macrocyclization were mainly composed of a complex mixture of cyclic and acyclic oligomers as revealed by MALDI-TOF MS analysis. Theoretical calculations (RM1) indicated a strain energy of 7.48 kcal/mol, which is comparable to that of cyclopentane (6.3 kcal/mol).<sup>9</sup> Such a small ring strain accounts for the preferential formation of the trimeric macrocycle to other possible cyclic oligomers. Nonetheless, tetramer and pentamer macrocycles were also detected from the crude product mixture of macrocyclization by means of MALDI-TOF MS analysis (see the Supporting Information). The formation of these higher cyclic oligomers, although disfavored by sharply increased ring strain, is not unprecedented for TTFV-based macrocyclophanes. In a previous report, Lorcý and co-workers also observed an inseparable mixture of tetrameric and pentameric macrocycles formed from electrolysis of a bis(dithiafulvenyl)benzene monomer.<sup>3c</sup>

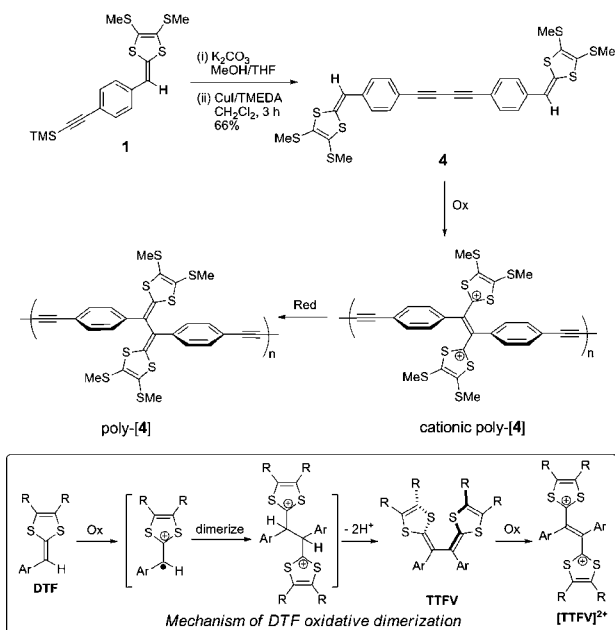
In addition to the macrocycle, a rodlike DTF end-capped diyne **4** was prepared from DTF **1** through a straightforward Hay coupling protocol depicted in Scheme 3. X-ray crystal-

(7) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320–3321.

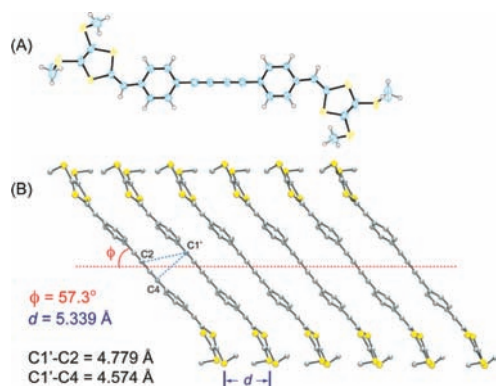
(8) A similar Cu(I)/Pd(II) co-catalyst system was previously reported in the synthesis of TTF-based [18]annulenes. See: Enozawa, H.; Hasegawa, M.; Takamatsu, D.; Fukui, K.; Iyoda, M. *Org. Lett.* **2006**, *8*, 1917–1920.

(9) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312–322.

**Scheme 3.** Synthesis of Bis(DTF)-End-Capped Diyne **4** and Related Polymers



lographic analysis (Figure 1)<sup>10</sup> reveals that the molecular structure of **4** assumes a  $D_2$  symmetry and in the crystal



**Figure 1.** (A) ORTEP drawing of diene **4** (30% probability thermal ellipsoids). (B) Crystal packing viewed along  $a$ -axis.

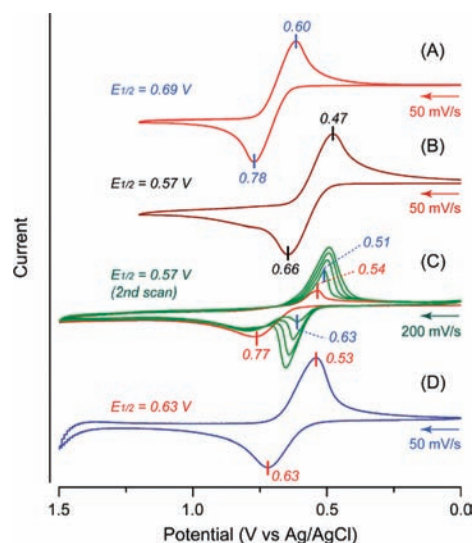
lattice the molecules are closely packed at a distance of  $d = 5.34 \text{ \AA}$  with an inclination angle  $\phi = 57.3^\circ$  between the axes of molecules and the packing axis. Such packing geometries are moderately deviated from the ideal arrangements in favor of diacetylene 1,4-addition ( $d = 4.9 \text{ \AA}$ ,  $\phi = 45^\circ$ ) polymer-

(10) Crystallographic data for diene **4**:  $C_{28}H_{22}S_8$ ,  $M_r = 614.96$ ; monoclinic; space group  $P2_1/c$  (no. 14);  $a = 5.352(9) \text{ \AA}$ ,  $b = 7.214(11) \text{ \AA}$ ,  $c = 35.96(6) \text{ \AA}$ ;  $\beta = 90.798(17)^\circ$ ;  $V = 1388(4) \text{ \AA}^3$ ;  $Z = 2$ ;  $\rho_{\text{calcd}} = 1.471 \text{ g cm}^{-3}$ ;  $\mu = 6.61 \text{ cm}^{-1}$ ;  $\lambda = 0.71075 \text{ \AA}$ ;  $T = 120 \pm 1 \text{ }^\circ\text{C}$ ;  $2\theta_{\text{max}} = 55.0^\circ$ ; total number of reflections collected = 8576;  $R_1 = 0.1143$  (2067 observed with  $I > 2(I)$ );  $wR_2 = 0.3590$  for 164 variables and 2299 unique reflections with ( $R_{\text{int}} = 0.0539$ ); residual electron density = 1.81 (0.06  $\text{\AA}$  from S3) to  $-0.74$  (0.90  $\text{\AA}$  from S2)  $e \text{ \AA}^{-3}$  (CCDC 749087).

ization,<sup>11</sup> suggesting a low probability of topochemically controlled polymerization.

On the other hand, diene **4** can be polymerized via a DTF dimerization approach as shown in Scheme 3. Such dimerization could be induced by either chemical or electrochemical means. Treatment of diene **4** with chemical oxidants such as molecular iodine in  $\text{CH}_2\text{Cl}_2$  was first attempted to effect polymerization. Under these conditions, diene **4** was found to quickly form an insoluble greenish product, which was then reduced by  $\text{Na}_2\text{S}_2\text{O}_3$  to afford a yellow solid. The resulting solid was soluble in  $\text{CH}_2\text{Cl}_2$ , and MALDI-TOF MS analysis showed that it contained a mixture of oligomers (oligo-[**4**]) ranging from dimer to octamer (see the Supporting Information).

Apart from the chemically induced polymerization, linear chain-like polymers (poly-[**4**]) were also acquired electrochemically. The cyclic voltammogram shown in Figure 2C



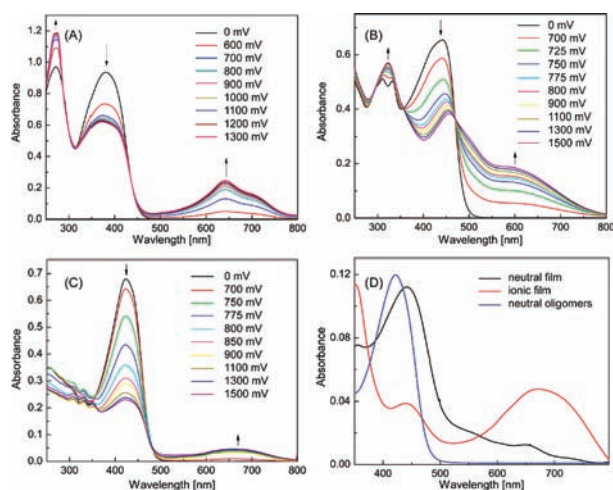
**Figure 2.** Cyclic voltammograms of (A) macrocycle **3**, (B) acetylenic TTFV **2**, (C) diene **4** in successive scans, and (D) thin film of poly-[**4**]. Key: supporting electrolyte,  $\text{Bu}_4\text{NBF}_4$  (0.1 M); solvent,  $\text{CH}_2\text{Cl}_2$ ; working electrode, glassy carbon; counter electrode, Pt; reference electrode, Ag/AgCl.

reveals the detailed electropolymerization processes of diene **4** on a glassy carbon electrode. On the first anodic scan, an irreversible wave is observed at  $+0.77 \text{ V}$  (vs Ag/AgCl) which is assigned to the oxidation of DTF into  $[\text{DTF}]^+$ . In the reverse sweeping process, a reversible cathodic peak emerges at  $+0.54 \text{ V}$ . On the second cycle of the CV scan, a reversible redox couple can be clearly seen at  $E_{\text{pa}} = +0.63 \text{ V}$  and  $E_{\text{pc}} = +0.51 \text{ V}$ . The half-wave potential of this wave pair is calculated as  $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2 = +0.57 \text{ V}$ , which is identical to that observed from acetylenic TTFV **2** (Figure 2B). This reversible redox couple is characteristic of a simultaneous bielectronic process on TTFV as a result of potential inversion.<sup>3b,d</sup> Moreover, the irreversible anodic peak

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at +0.77 V is found to diminish with increasing scan cycles. These results clearly indicate the formation of TTFV moieties and the depletion of DTF groups during successive CV scans. As the number of scan cycles increases, the intensity of the redox couple due to TTFV grows steadily, which is indicative of the growth of a conducting polymer film on the electrode. Also of note is that the redox couple gradually shifts to quasi-reversible behavior with increasing ( $E_{pa} - E_{pc}$ ) separation. Figure 2D shows the cyclic voltammogram of the thin film of poly-[4] obtained after 100 scans (switching points were set at 0.0 and +1.50 V) on a glassy carbon electrode. The absence of an irreversible DTF oxidation wave signifies complete electropolymerization. The half-wave potential of poly-[4] is observed at  $E_{1/2} = +0.63$  V, which is anodically shifted relative to that of TTFV **2**. Such a shift can be rationalized as resulting from increased steric crowding, as some of the TTFV moieties on the extended polymer backbone are constrained in a *cisoid*-like conformation upon oxidation. This is evident from the much higher half-wave potential observed for macrocycle **3** ( $E_{1/2} = +0.69$  V, Figure 2A), in which all the TTFV moieties are constrained to pseudo-*cisoid*, in comparison to that of ring strain-free TTFV **2**.

UV-vis spectroelectrochemical analysis was carried out on the TTFV derivatives to probe their electronic characteristics. In the experiments, a UV-vis spectral scan was performed after the electrolysis of an analyte at a controlled voltage for at least 90 s to ensure the electric current attained a constant value. As such, the systems examined by UV-vis spectroscopy can be deemed as having arrived at equilibrium.



**Figure 3.** UV-vis spectral changes associated with varying applied potentials during the electrolysis of (A) acetylenic TTFV **2**, (B) macrocycle **3**, and (C) diyne **4**. Key: supporting electrolyte,  $\text{Bu}_4\text{NBF}_4$  (0.1 M); solvent,  $\text{CH}_2\text{Cl}_2$ ; working electrode, glassy carbon; counter electrode, Pt; reference electrode, Ag/AgCl. (D) UV-vis spectra of poly-[4] thin film in neutral and cationic states and oligo-[4] in  $\text{CH}_2\text{Cl}_2$ .

As can be seen from Figures 3A–C, compounds **2–4** all show diminished high energy  $\pi \rightarrow \pi^*$  absorption concomitant with a steadily growing low-energy band ranging from

ca. 500 to 800 nm with increasing applied potential. The low-energy band is attributed to the  $[\text{TTFV}]^{2+}$  generated upon oxidation. Of particular interest is the electronic absorption behavior of the thin film of poly-[4], which was electrochemically deposited on an indium tin oxide (ITO) coated glass substrate by repetitive CV scans in the range of 0.0 to +1.50 V for 50 cycles. The resulting polymer film was greenish yellow and semitransparent in appearance after thorough rinsing with solvents to remove electrolyte and other soluble contents. The poly-[4] film prepared in this way was almost neutral. Its UV-vis spectrum shown in Figure 3D has a prominent  $\pi \rightarrow \pi^*$  absorption band at 441 nm and a long absorption tail extending from ca. 520 to 750 nm. Compared with the absorption profile of oligo-[4] prepared through chemical oxidation–reduction procedures, the long-wavelength absorptions in the spectrum of neutral poly-[4] film can be ascribed to the unreduced  $[\text{TTFV}]^{2+}$  moieties remaining on the film after electrodeposition. The polymer film could be recharged at +0.90 V for 1.0 min in an electrolysis setup in the presence of a blank electrolyte solution (0.1 M  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_2\text{Cl}_2$ ). Upon charging, the thin film could be visibly seen gradually changing color from yellow to dark green. UV-vis spectral analysis shows that the positively charged film of poly-[4] gives a strong broad absorption band in the spectral region of ca. 550 to 800 nm with  $\lambda_{\text{max}}$  at 665 nm. The absorption band at 441 nm, however, becomes much weaker in intensity.

In conclusion, we have demonstrated the synthetic versatility of an acetylenic phenyldithiafulvene synthon **1**. By taking advantage of the electrochemical switching behavior as well as the dual reactivity imparted by the DTF and acetylenic groups, macrocyclophane and linear polymers have been prepared through concise synthetic routes. An intriguing finding was made on diyne **4**, which offers a convenient monomer for electropolymerization leading to TTFV-embedded polymer thin films on conductive substrates. The redox coloration behavior of poly-[4] manifested in Figure 3D suggests appealing application in organic electrochromic devices operating in the near-IR region.<sup>12</sup>

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**Supporting Information Available:** Synthetic details and spectroscopic data for new compounds, theoretical calculations on **2** and **3**, thermal analysis and the CIF file of diyne **4** (CCDC 749087). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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