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Planar Acetylene-Expanded TTFAQ Analogues

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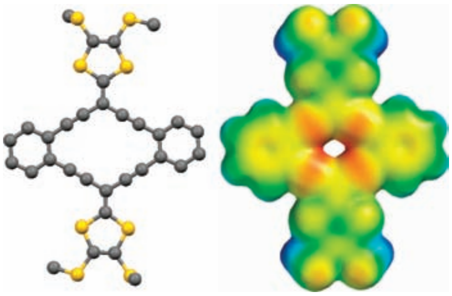
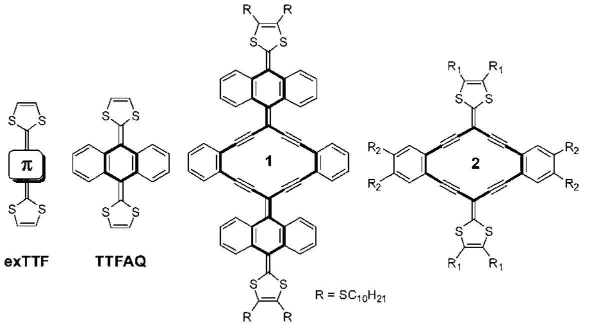
ABSTRACT



Two planar acetylene-expanded TTFAQ analogues (8a and 8b) were synthesized through a one-pot, 4-fold Sonogashira coupling protocol. The structure and electronic properties of these compounds were investigated by single-crystal X-ray crystallography, UV−vis spectroscopy, and cyclic voltammetry.

Tetrathiafulvalene (TTF) analogues bearing extended conjugated π-spacers, namely π-extended TTFs (exTTFs), are important building blocks for organic electronic materials and supramolecular chemistry.[1] A popular strategy to design ex-TTFs is accomplished by insertion of various conjugated π-units in between the dithiole rings of a parent TTF structure as illustrated in Scheme 1. Among numerous motifs explored in the literature, the TTF analogues that are expanded through an anthraquinoid type of spacer (generally referred to as TTFAQs) have received considerable attention, owing to their remarkable electron-donating ability facilitated by the unique gaining of aromaticity at the central anthracene unit upon two-electron oxdiation.[1d,2] Further π-extended variants of TTFAQs are less frequently addressed in the literature; however, they afford very appealing molecular systems that challenge the mindsets of both synthetic and theoretical chemists.[3] In 2008, our group reported a highly expanded TTFAQ analogue **1**, in which an enyne macrocycle together with two anthraquinodimethane moieties constituted the π-spacer.[4] The central macrocyclic enyne framework of

Scheme 1. Structures of TTFAQ and π-Extended TTFAQs[a]



[a] The central cyclic π-bridges are highlighted in bold.

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(1) For recent reviews on exTTFs, see: (a) Bryce, M. R. *J. Mater. Chem.* **2000**, *10*, 589. (b) Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372. (c) *TTF Chemistry: Fundamentals and Application of Tetrathiafulvalene*; Yamada, J., Sugimoto, T., Eds.; Springer Verlag: Heidelberg, 2004. (d) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891. (e) Frère, P.; Skabara, P. J. *Chem. Soc. Rev.* **2005**, *34*, 69. (f) Roncali, J. *J. Mater. Chem.* **1997**, *7*, 2307.

(2) (a) Bryce, M. R.; Moore, A. J. *Tetrahedron Lett.* **1988**, *29*, 1075. (b) Akiba, K.; Ishikawa, K.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2674.

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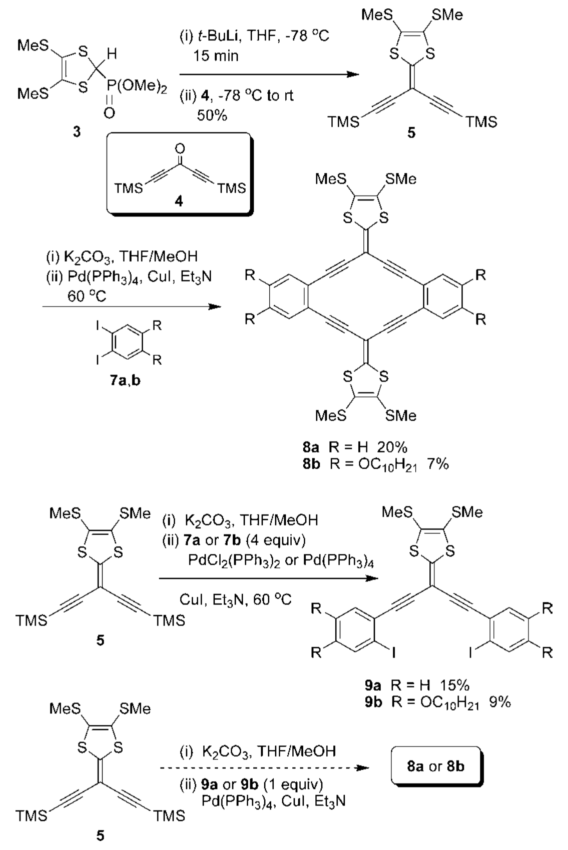
exTTF **1** represents the first example of a peculiar type of radia[*n*]annulenes,[5] the structure and properties of which have invoked a series of questions both fundamentally and practically important; for instance: (1) Will the central radiaannulene π-bridge show the gaining of aromaticity similar to that of TTFAQ upon oxidation?[6] (2) Will the incorporation of π-extension add new dimensions for control over solid-state ordering, multistage-redox behavior, and supramolecular stacking in solution or the solid state?[1] (3) Will enhanced electronic and photonic performances be achievable through this new design concept? To address these issues, synthetic access to macrocyclic enyne bridged TTFAQ analogues is prerequisite.

Strictly speaking, exTTF **1** does not serve as an adequate model for the study of π-expanded TTFAQ systems, since unlike TTFAQs and other exTTFs the two dithiole rings of **1** have no electronic communication through the long π-spacer as a result of its nonplanar, *S*-shaped π-framework.[4] The structural nonplanarity of **1** arises mainly from the significant steric crowdedness among the anthraquinone and macrocyclic enyne moieties. To circumvent this setback, we then revised our design to a simpler motif, exTTF **2** (Scheme 1), which can be viewed as an expanded version of TTFAQ derived from directly inserting acetylenic units into the quinoid spacer of TTFAQ. In principle, motif **2** should afford a better model system than exTTF **1** because its π-framework is absent of any steric hindrance and hence capable of taking a planar ground-state structure in favor of maximal π-conjugation.

The key step in the synthesis of exTTF **2** is to construct the central macrocyclic enyne moiety. This can be accomplished through a one-pot, 4-fold Sonogashira cyclization protocol developed by our group in the synthesis of exTTF **1**.[4] Following this strategy, two acetylene-expanded TTFAQs **8a** and **8b** were prepared as outlined in Scheme 2. The synthesis began with a Wittig−Horner reaction between ketone **4** and the ylide in situ generated by treatment of phosphonate **3** with *t*-BuLi. Dithiole precursor **5**[7] was obtained in a modest yield and was desilylated with K_2CO_3 to give corresponding terminal alkyne. This intermediate showed relatively low stability and was immediately subjected to Sonogashira coupling with diiodobenzene **7a** or **7b** under dilute conditions (ca. 4−6 mM). To our delight, the two macrocyclization reactions successfully afforded the desired products. After column chromatographic separation, expanded TTFAQs **8a** and **8b** were obtained in 20% and 7% yield, respectively. Given the fact that the macrocyclization underwent four consecutive steps of cross-coupling reactions in one pot, the yields of **8a**,**b** are actually very reasonable.[8]

Scheme 2. Synthesis of Acetylene-Expanded TTFAQs **8a** and **8b**



Parallel to the one-pot approach, the synthesis of **8a** and **8b** through a stepwise route was also explored. As outlined in Scheme 2, desilylation of dithiole precursor **5** followed up by cross coupling with excess diiodobenzene **7a** or **7b** afforded precursors **9a** and **9b**. With **9a** and **9b** in hand, another iteration of intramolecular 2-fold Sonogashira coupling would furnish the desired products **8a** and **8b**. This synthetic route, however, was proven inefficient due to the sluggish yield of the first coupling step. Further attempts at macrocyclization through this approach were therefore abandoned.

The molecular structures and purity of expanded TTFAQ analogues **8a**,**b** and relevant precursors were unambiguously

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[3] (a) Martín, N.; Sánchez, L.; Seoane, C.; Ortí, E.; Viruela, P. M.; Viruela, R. *J. Org. Chem.* **1998**, *63*, 1268. (b) Moore, A. J.; Bryce, M. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 157.

[4] Chen, G.; Wang, L.; Thompson, D. W.; Zhao, Y. *Org. Lett.* **2008**, *10*, 657.

[5] (a) Tykwinski, R. R.; Gholami, M.; Eisler, S.; Zhao, Y.; Melin, F.; Echegoyen, L. *Pure Appl. Chem.* **2008**, *80*, 621. (b) Gholami, M.; Melin, F.; McDonald, R.; Ferguson, M. J.; Echegoyen, L.; Tykwinski, R. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 9081. (c) Mitzel, F.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Helv. Chim. Acta* **2004**, *87*, 1130. (d) Mitzel, F.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Chem. Commun.* **2003**, 1634. (e) Gholami, M.; Chaur, M. N.; Wilde, M.; Ferguson, M. J.; McDonald, R.; Echegoyen, L.; Tykwinski, R. R. *Chem. Commun.* **2009**, 3038.

[6] The macrocycle enyne framework in **1** and **2** presents a new addition to a class of *carbo*-meric molecules that have attracted great interest in terms of π-delocalization and aromaticity in neutral and ionized states. See: (a) Lepetit, C.; Nielsen, M. B.; Diederich, F.; Chauvin, R. *Chem.*−*Eur. J.* **2003**, *9*, 5056. (b) Lepetit, C.; Godard, C.; Chauvin, R. *New. J. Chem.* **2001**, *25*, 572. (c) Godard, C.; Lepetit, C.; Chauvin, R. *Chem Commun.* **2000**, 1833. (d) Chauvin, R. *Tetrahedron Lett.* **1995**, *36*, 397.

[7] Analogues of **5** with different substituents were previously reported; see: (a) Nielsen, M. B.; Moonen, N. N. P.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Chem. Commun.* **2001**, 1848. (b) Nielsen, M. B.; Petersen, J. C.; Thorup, N.; Jessing, M.; Andersson, A. S.; Jepsen, A. S.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M. *J. Mater. Chem.* **2005**, *15*, 2599.

[8] The yield of **8a** (20%) corresponds to an average yield of 67% for each individual Sonogashira coupling, while the yield of **8b** (7%) corresponds to 51% yield for each individual coupling.

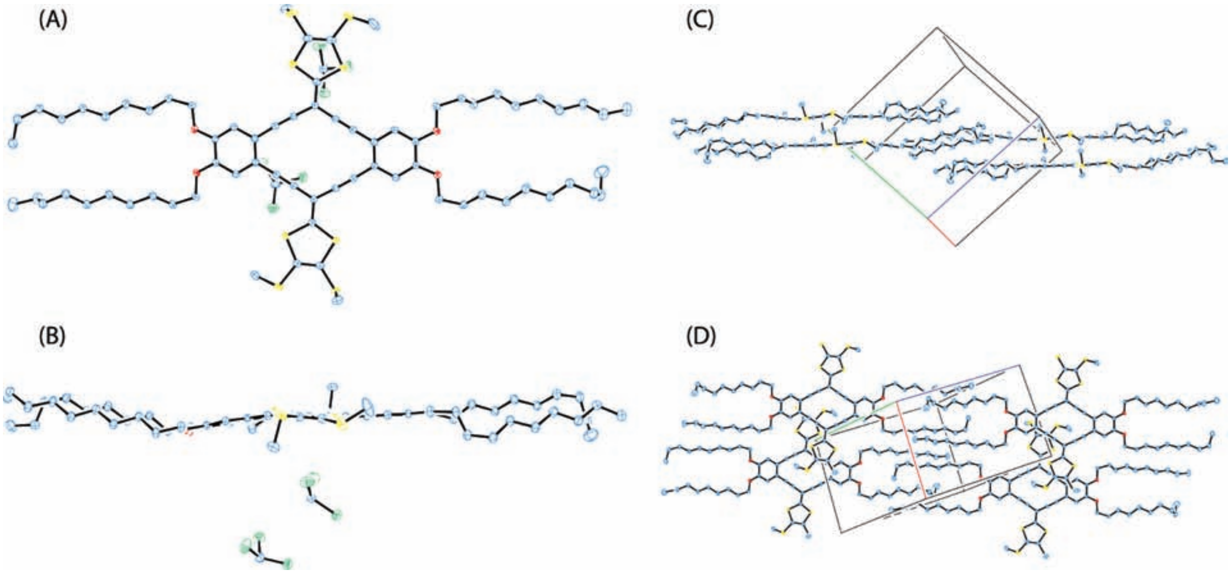

Figure 1. Single-crystal structure of compound **8b**: (A) front view of ORTEP plot, (B) side view of ORTEP plot, (C) side view of crystal packing diagram, and (D) front view of crystal packing diagram. Ellipsolid probability at 30% level. Note that solvent $CHCl_3$ molecules are present in the ORTEP plots.

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characterized by NMR, MS, and IR analyses (see the Supporting Information). Compound **8b** shows much better solubility in common organic solvents than **8a** due to the presence of solubilizing decyloxy chains. Single crystals of **8b** were successfully grown by slow evaporation of the solution of **8b** in $CHCl_3/CH_3CN$ (4:1, v/v) in the presence of Bu_4NBF_4 at ca. 4 °C. With these crystals, the solid-state structure properties of **8b** were elucidated by means of single-crystal X-ray crystallography.The single-crystal structure of **8b** is depicted in Figure 1A,B, in which a coplanarity of the central enyne macrocycle with adjacent phenyl and dithiole rings is clearly seen. Of note is that the central enyne macrocycle of **8b** has geometric parameters similar to those observed in the crystal structure of exTTF **1**.[4] A closer comparison of the two sets of crystallographic data, however, shows that the bond length alternation (BLA) index (δ_{BLA})[9] of **8b** (0.155 Å) is slightly shorter than that of exTTF **1** (δ_{BLA} = 0.165 Å). The variation in BLA suggests that the cyclic enyne segment in **8b** possesses a higher degree of π-delocalization than exTTF **1**, resulting from stronger electronic interactions between the dithiole rings and the central enyne macrocycle.

A very intriguing aspect of the solid-state structure of **8b** lies in its crystal packing geometry, which stands in contrast to that of nonplanar exTTF **1**.[4] As shown in Figure 1C,D, the molecules of **8b** pack in a columnar fashion in the crystal, where the electron-rich dithiole rings directly overlap with the relatively electron-deficient macrocyclic enyne units, affording a slipped face-to-face stacking. The distance between the mean planes of two adjacent molecules is measured at 3.729 Å, and the close proximity between the donor (dithiole) and acceptor (enyne ring) is suggestive of intermolecular charge-transfer interactions.[10] Apparently, the planar framework of **8b** is key to the formation of efficient $\pi-\pi$ stacking in the solid state, which is expected to add benefit for electronic and optoelectronic applications.[11]

The electronic properties of TTFAQ analogues **8a** and **8b** were investigated by UV−vis and fluorescence spectroscopy. Figure 2A gives the normalized UV−vis absorption spectra for compounds **8a**, **8b**, and precursor **5** measured in $CHCl_3$. Compound **8a** shows two characteristic low-energy absorption bands at 480 and 453 nm, which are nearly identical to those of **8b** at 483 and 457 nm. These absorptions are substantially red-shifted in comparison to the maximum absorption band (λ_{max}) of dithiole precursor **5**, corroborating the presence of significant electronic interactions between the dithiole rings and the central macrocyclic enyne units in **8a** and **8b**. The fluorescence spectra for **8a** and **8b** are shown in Figure 2B, where both compounds exhibit a similar broad and structureless emission profile. The maximum emission wavelength (λ_{em}) of decyloxy chain attached exTTF **8b** appears at 510 nm, which is slightly blueshifted relative to that of **8a** at 522 nm.

Electrochemical redox behavior of compound **8b** was studied by cyclic voltammetry (CV), whereas efforts to characterize **8a** by CV failed due to limited solubility. Figure 3 shows the cyclic voltammograms of **8b** determined in

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[9] δ_{BLA} is determined based on the formula $\delta_{BLA} = R_s - R_m$, where R_s and R_m denote the average bond distances for C−C single bonds and multiple bonds on the macrocyclic enyne framework. The crystallographic data for **1** and **8b** can be found at Cambridge Crystallographic Data Centre (CCDC). Deposition numbers: 680314 and 726951.

[10] The electrostatic potential surface for **8a** was calculated at the B3LYP/6-31G(d) level of theory using the Spartan'06 program. The drawing in the graphical abstract shows that the highest electron density is concentrated at the dithiole rings, while the lowest electron density at the central enyne macrocycle unit.

[11] Yamada, J.-i.; Akutsu, H.; Nishikawa, H.; Kikuchi, K. *Chem. Rev.* **2004**, *104*, 5057.

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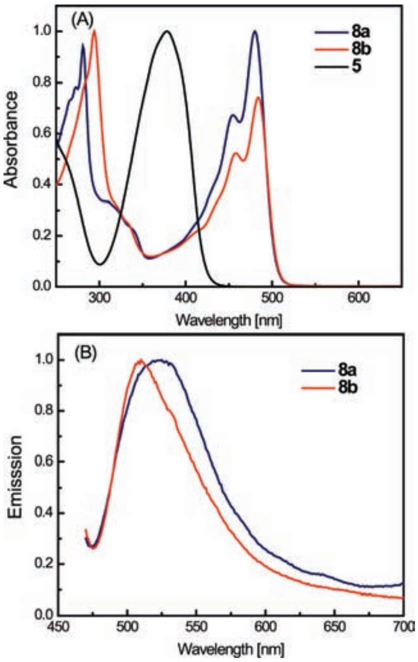

Figure 2. (A) Normalized UV−vis absorption spectra for **8a**, **8b**, and **5** measured in $CHCl_3$. (B) Normalized fluorescence spectra for **8a** and **8b** measured in $CHCl_3$ (λ_{ex} = 400 nm).

varied ranges of potential scan at 0 °C. In the scan range of −0.5 to +0.72 V, the voltammogram shows a pair of redox waves at $E_{pa}{}^1$ = 0.67 V and $E_{pc}{}^1$ = 0.53 V. Given the fact that the separation between the two peaks is 0.11 V and the peak positions are scan rate dependent, this redox wave pair is reckoned quasi-reversible and its origin is tentatively assigned to a simultaneous two-electron oxidation at the dithiole rings of **8b**. Of note is that the value of the first oxidation potential ($E_{pa}{}^1$) is similar to those reported for TTFAQs,[12] but much lower than that of nonplanar exTTF **1** ($E_{pa}{}^1$ = 0.98 V).[4] This result suggests that the acetylene expanded macrocyclic bridge in **8b** mediates electronic communication between the two dithiole rings to an extent that is comparable to the quinoid bridge in a typical TTFAQ. When scanned from −0.5 to +0.9 V, a second anodic current peak emerges at $E_{pa}{}^2$ = 0.76 V, which is associated with a relatively sharp cathodic current peak at $E_{pc}{}^2$ = 0.65 V. When the switching potentials are expanded from −0.5 to +1.2 V, two anodic peaks at 0.64 and 0.76 V along with one broad cathodic peak at 0.62 V are observed in the voltammogram. In the scan range of −0.5 to +1.5 V, a third anodic peak at 1.32 V appears, while there is no noticeable cathodic current observed in the voltammogram. The irreversible pattern here may be rationalized by an EC mechanism, where an electrochemically promoted reaction[13] swiftly follows up the oxidation of **8b**. Differential pulse voltammetric analysis (see the inset of Figure 3) also corroborates that **8b** undergoes three distinct oxidation processes at 0.59, 0.71, and 1.13 V, respectively. Investigations on the detailed electrochemical mechanisms are currently underway, and the results will be reported in due course.

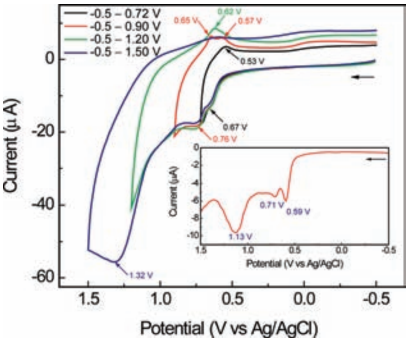

Figure 3. Cyclic voltammograms of **8b** measured in varied potential scan windows at 0 °C: solvent, CH_2Cl_2; electrolyte, Bu_4NBF_4 (0.1 M); working electrode, glassy carbon; counter electrode, Pt; reference electrode, Ag/AgCl; scan rate, 0.5 V/s. Inset: differential pulse voltammogram of **8b** measured at 0 °C.

In conclusion, we have presented the synthesis and characterization of the first examples of planar acetylene-expanded TTFAQ analogues. It is worth remarking that the one-pot Sonogashira cyclization protocol was again proven to be very efficient in constructing shape-persistent macrocyclic enyne structures. These planar acetylene-expanded TTFAQ analogues, in view of their efficient solid-state packing and electrochemical activities, may deliver useful applications in TTF based organic electronic materials and devices.

Acknowledgment. We thank NSERC Canada, Canada Foundation for Innovation (CFI), and Industrial Research and Innovation Fund (IRIF) for funding.

Supporting Information Available: Synthetic procedures and spectroscopic characterization for all new compounds and crystallographic data for **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Christensen, C. A.; Batsanov, A. S.; Bryce, M. R. *J. Org. Chem.* **2007**, *72*, 1301.

(13) An electrochemically induced 1,5-cyclization of the endiyne segments at the central macrocycle is speculated to be involved. See: Ramkumar, D.; Kalpana, M.; Varghese, B.; Sankararaman, S. *J. Org. Chem.* **1996**, *61*, 2247.