Tetrahedron Letters 51 (2010) 6552–6556

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis and properties of TTFV-hinged molecular tweezers

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ARTICLE INFO

Article history:
Received 8 September 2010
Revised 2 October 2010
Accepted 6 October 2010
Available online 14 October 2010

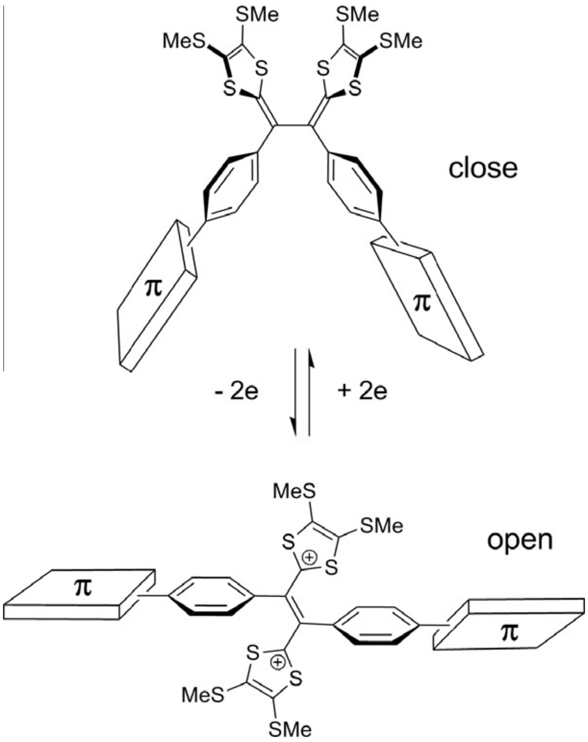
ABSTRACT

Two molecular tweezers containing a tetrathiafulvalene vinylogue (TTFV) core were synthesized via sequential Sonogashira and Horner–Wadsworth–Emmons (HWE) reactions. The electrochemical and spectroscopic properties of these TTFV tweezers were investigated by UV–vis absorption spectroscopy, cyclic voltammetry, and spectro-electrochemical measurements. The property characterizations suggest potential application in electrochemically-actuated molecular switching devices.

Tetrathiafulvalene (TTF) derivatives aside from their traditional use for organic conducting materials[1] have recently attracted growing attention as building blocks for stimuli-responsive molecular devices such as sensors, switches, and logic gates.[1a,2] Of numerous TTF derivatives, diaryl-substituted vinylogous tetrathiafulvalene (TTFV) shows unique conformational switching property associated with a simultaneous two-electron redox reaction occurring on the TTFV moiety.[3] Upon oxidation the TTFV scaffold changes from cis to trans conformation as a result of significant electrostatic repulsion between the two dithiolium rings. This switching process is rapid, reversible, and readily actuated by electrochemical or chemical inputs. Taking advantage of this property, a number of TTFV-based switchable ligands for metal cations has been previously prepared and investigated.[2a,3c,4] Most recently, our group reported the use of a simple acetylenic TTFV precursor to selectively construct two distinct types of TTFV-macromolecules, shape-persistent macrocycles and linear polymers, wherein the conformational switching of TTFV dictating the synthetic consequences.[5]

The unique switching property of diaryl-substituted TTFV led us to envisage its usefulness as a molecular hinge for electrochemically-actuated molecular tweezers.[6] To further explore this concept, we designed a new type of TTFV molecular tweezers. As shown in Scheme 1, two π-conjugated functional groups are enlisted as the 'tips' of tweezers, which are connected to a central TTFV core through rigid covalent linkage. In principle, such TTFV tweezers would assume a stable V-like molecular shape in the neutral state, giving a 'close' form in which the π-tips are spatially close enough to allow co-operative 'griping' of a guest molecular species through non-covalent forces such as π-stacking or charge-transfer interactions. Upon oxidation, the TTFV molecular hinge would rotate into a linear trans orientation, thus 'opening' the molecular tweezers to release the guest. Given the remarkable electronic properties of TTFV,[3–5] the molecular tweezers are accordingly envisioned to exhibit easy controllability and versatile adaptability for the preparation of functional molecular switching devices.

Prior to testing the tweezer-like behavior, proof-of-concept model compounds need to be prepared. In this Letter, we report the synthesis and molecular properties of two TTFV-hinged molecular tweezers, the tip regions of which were designed to



Scheme 1. General structure of TTFV-hinged molecular tweezers.

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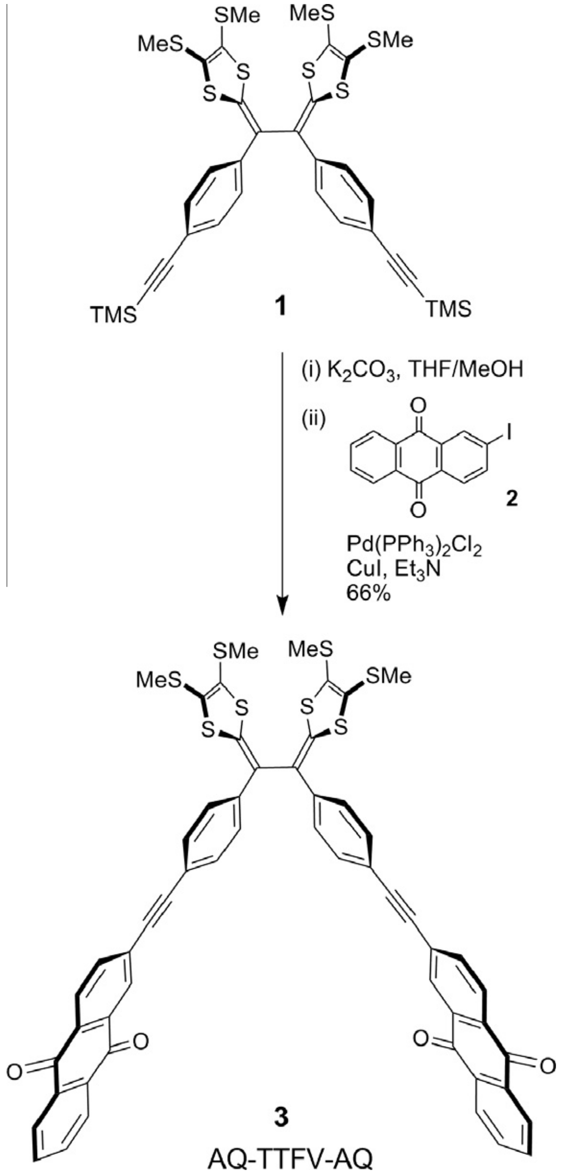
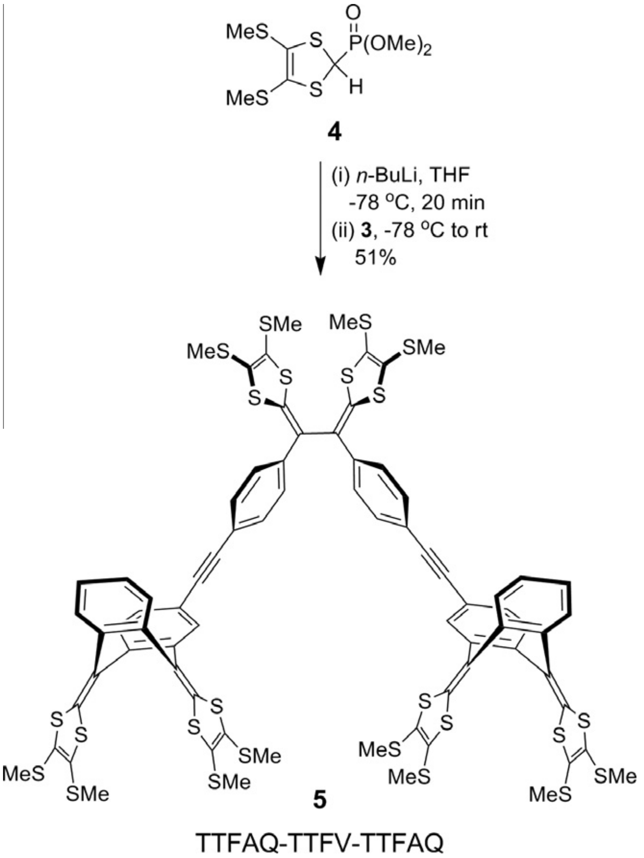
doi:10.1016/j.tetlet.2010.10.032



Scheme 2. Synthesis of AQ-TTFV-AQ **3** by Sonogashira coupling.

be anthraquinone (AQ) or anthraquinoid-type π-extended tetrathiafulvalene (TTFAQ), respectively. In the ground state, the AQ group has a planar π-framework, whereas TTFAQ takes a saddle-like structure.[7] Given the rich electronic properties of AQ and TTFAQ, the two designed molecular tweezers are thus expected to show supramolecular interactions with certain aromatic species via π-stacking and charge-transfer forces. Moreover, the tweezers are donor/acceptor molecular arrays that may find applications in organic electronic materials and molecular switching devices.[7]

Scheme 2 illustrates the synthesis of AQ-tipped molecular tweezers **3**. Acetylenic TTFV precursor **1** was first prepared through the method we previously reported.[5] Removal of the trimethylsilyl groups in TTFV **1** with K_2CO_3, followed by Sonogashira coupling with 2-iodoanthraquinone (**2**), afforded molecular tweezers **3** in 66% yield. Note that compound **3** is an acceptor–donor–acceptor triad in electronic structure and hence is referred to as AQ-TTFV-AQ in the following discussions. With compound **3** in hand, the targeted TTFAQ-tipped tweezers were supposed to be readily obtained through a twofold Horner–Wadsworth–Emmons (HEW) reaction.

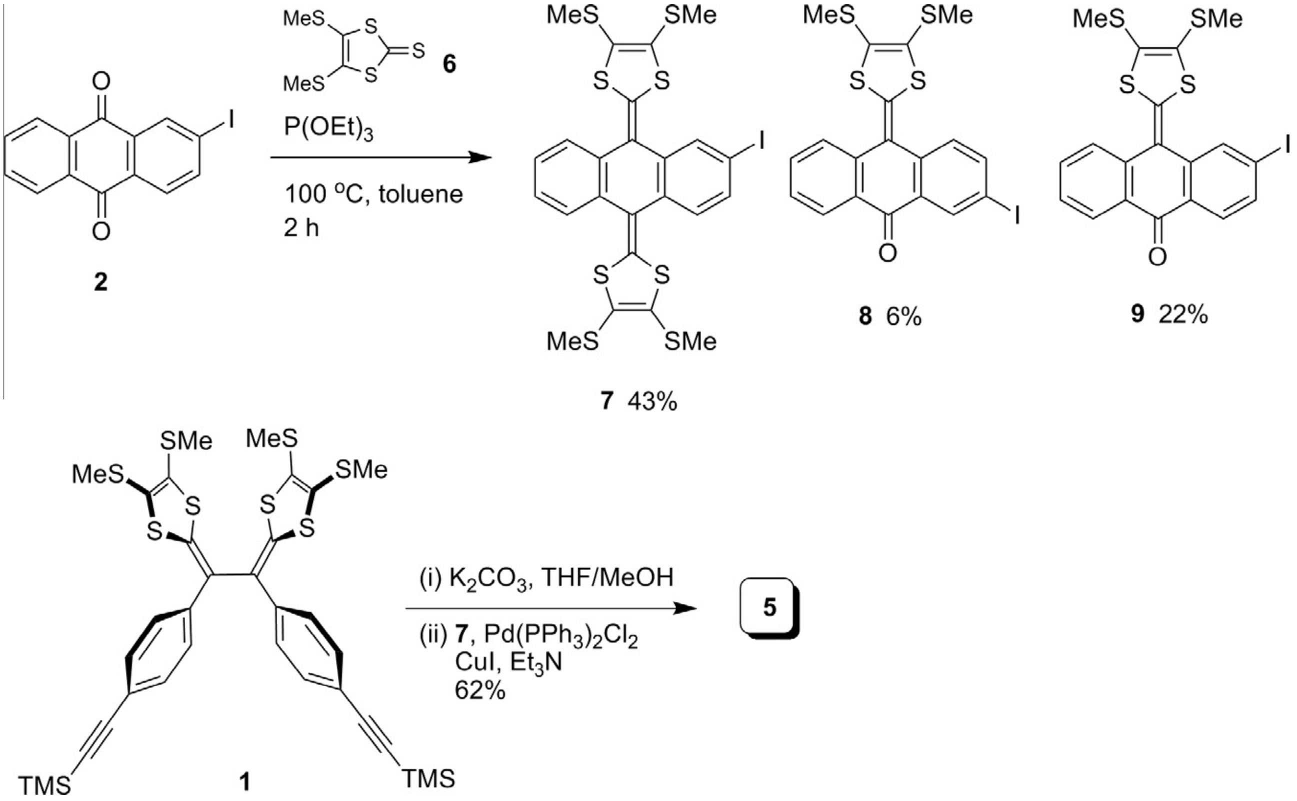


Scheme 3. Synthesis of TTFAQ-TTFV-TTFAQ **5** by HWE reaction.

As shown in Scheme 3, phosphonate **4**[8] was first treated with a strong base, *n*-BuLi, at low temperature to form phosphonate ylide. AQ-TTFV-AQ **3** was next added to react with the in situ generated phosphonate ylide, affording the desired molecular tweezers **5** which is a TTFAQ-TTFV-TTFAQ triad. The HWE reaction produced **5** in reasonable yields; however, purification of **5** by column chromatography was found tedious and tricky. Compound **5** tends to decompose slowly in contact with silica gel. As a result, the isolated yield of **5** often showed significant variation as a function of the duration of column chromatographic separation.

In addition to the HWE strategy, we have also tried an alternative Sonogashira coupling route to synthesize compound **5**. As shown in Scheme 4, a mono-iodo substituted TTFAQ precursor **7** was first prepared by a $P(OEt)_3$-promoted olefination reaction[9] between 2-iodoanthraquinone **2**[8c] and thione **6**[8] in toluene at 100 °C. The reaction gave the desired product **7** in 43% yield, along with the formation of two byproducts **8** and **9** resulting from incomplete olefination. All these compounds were readily separated and purified by column chromatography. Cross-coupling of **7** with desilylated TTFV **1** under the catalysis of Pd/Cu in Et_3N afforded compound **5**, which precipitated out during the reaction. The crude product could then be easily purified by flushing through a short silica plug with $CHCl_3$, giving pure **5** in a yield of 62%. The short separation procedure considerably reduced the undesirable decomposition of **5** when exposed to silica gel, therefore, ensuring more consistent and reproducible yields for this reaction.

The molecular structures of TTFV-hinged tweezers **3** and **5** were characterized by IR, NMR, and MS analyses.[10] The electrochemical redox properties of **3**, **5**, and TTFV precursor **1** were investigated by cyclic voltammetry (CV), and detailed cyclic voltammograms are given Figure 1.



Scheme 4. Synthesis of TTFAQ-TTFV-TTFAQ **5** by Sonogashira coupling.

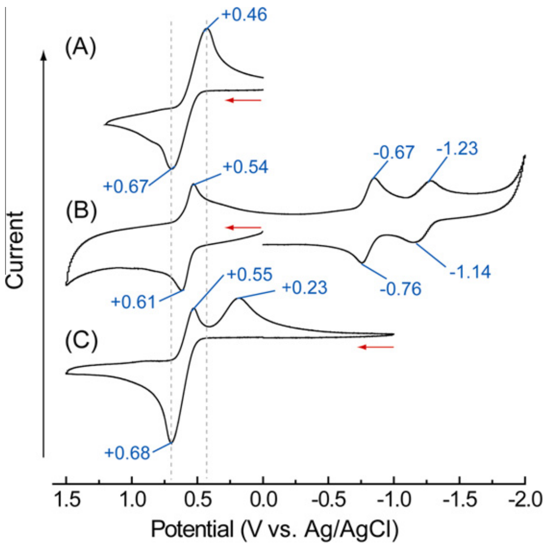


Figure 1. Cyclic voltammograms of (A) TTFV **1**, (B) AQ-TTFV-AQ **3**, and (C) TTFAQ-TTFV-TTFAQ **5**. Experimental conditions: analyte (ca. 10^{-3} M); Bu_4NBF_4 (0.1 M) as supporting electrolyte; CH_2Cl_2 as solvent; glassy carbon as working electrode; Pt wire as counter electrode; Ag/AgCl as reference; scan rate 0.1 V s^{-1}.

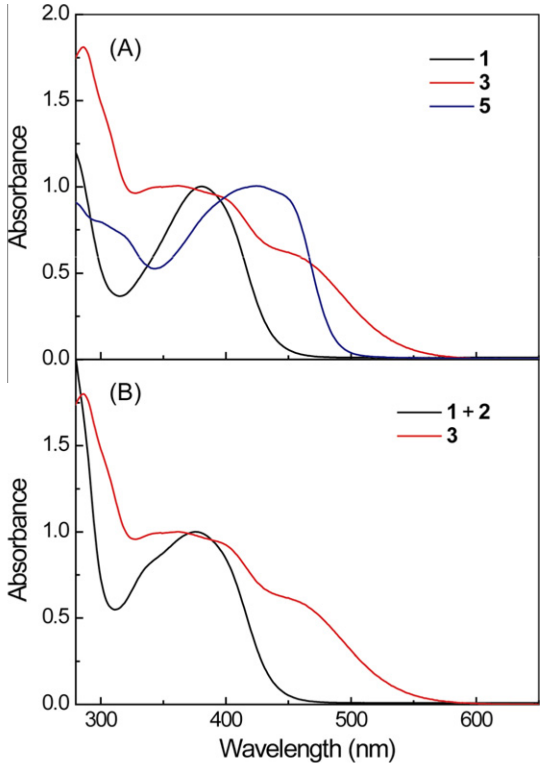


Figure 2. (A) UV–vis absorption spectra of **1**, **3**, and **5** measured in CH_2Cl_2. (B) UV–vis spectrum of **3** comparing against the spectrum of mixture of **1** and **2** (in 1:2 molar ratio).

From Figure 1A, it can be seen that TTFV **1** gives a reversible redox couple at E_{pa} = +0.67 V and E_{pc} = +0.46 V, which are attributed to a simultaneous two-electron process. In the CV profile of AQ-TTFV-AQ **3** (Fig. 1B), the TTFV-originated redox wave pair is significantly shifted relative to TTFV **1**. The E_{pa} value is shifted to less positive direction at +0.61 V, while E_{pc} to more positive potential at +0.54 V, indicating increased electrochemical reversibility. The formal oxidation potential $(E_{pa} + E_{pc})/2$ of **3** (+0.58 V) is observed to be slightly greater than that of TTFV **1** (+0.57 V), as a result of the electron-withdrawing effect of the AQ groups on the TTFV unit in **3** through π-conjugation.[2m,8c,d] In the negative potential window, two reversible redox wave pairs are observed, which are typical of the successive two-step reduction of AQ and indicate no electronic communication between the two AQ groups.[8c] Of interest is the cyclic voltammogram of TTFAQ-TTFV-TTFAQ **5** (Fig. 1C). In the anodic scan, only one oxidation peak is observed at +0.68 V. The current intensity of this peak suggests it arise from simultaneous oxidation at the central TTFV and the two TTFAQ moieties involving total 6 electrons. In the cathodic scan, however, two reduction peaks are seen at +0.55 V and +0.23 V, respectively. The former is likely due to the reduction of the central TTFV unit, while the latter corresponds to the reduction of the two TTFAQ moieties. The CV patterns of **5** reveal a significant degree of electronic contact between the TTFV and TTFAQ groups within the molecule.

The electronic absorption properties of molecular tweezers **3** and **5** were investigated by UV–vis absorption spectroscopy. Figure 2A compares the absorption spectra of **1**, **3**, and **5**. TTFV **1** shows an absorption band at 380 nm in the low-energy region. In the spectrum of AQ-TTFV-AQ **3**, a notable absorption shoulder at 460 nm along with broad long-wavelength absorption tail extending to ca. 580 nm is observed. To clarify the origin of this band, UV–vis spectrum of a 1:2 mixture of TTFV **1** and AQ **2** was determined and compared with the spectrum of **3** (Fig. 2B). The absence of such a low-energy absorption band in the UV–vis profile of the mixture of **1** and **2** confirms that the long-wavelength shoulder and tail in the spectrum of **3** is due to intramolecular charge transfer (ICT). This conclusion is in agreement with the CV results, indicating very significant electronic interaction between the TTFV and AQ moieties through acetylenic linkage. The absorption spectrum of TTFAQ-TTFV-TTFAQ **5** shows a broad low-energy band peaking at 416 nm, the origin of this band can be assigned to overlapped $\pi \rightarrow \pi^*$ transition bands of TTFV and TTFAQ.[8c,d]

To gain a deeper insight into the redox process, UV–vis spectro-electrochemical analyses were performed on compounds **1**, **3**, and **5**. Detailed experimental results are shown in Figure 3. The absorption band of TTFV **1** at 380 nm is observed to decrease with increasing applied potential (Fig. 3A). In the meantime, a new long-wavelength absorption band emerges with a peak at 642 nm and a shoulder at 713 nm. This band is ascribed to the characteristic absorption of dication $[TTFV]^{2+}$. In the spectro-electrochemical measurements of AQ-TTFV-AQ **3**, a similar long-wavelength band is observed to grow with increasing applied potential, indicating the formation of $[TTFV]^{2+}$. The ICT band of **3** at 380 nm is observed to steadily reduce as the oxidation of TTFV progresses, while the absorption due to AQ at ca. 360 nm remains unchanged. For TTFAQ-TTFV-TTFAQ **5**, a broad band peaking at 650 nm grows with increasing applied potential. Concomitantly, the absorption band at 416 nm shows a significant decrease and a band at ca. 330 increases notably. According to the CV data, the spectral changes in Figure 3C are attributed to the simultaneous formation of $[TTFV]^{2+}$ and $[TTFAQ]^{2+}$ in compound **5** during electrolysis. Overall, the spectro-electrochemical studies corroborate that the TTFV units in molecular tweezes **3** and **5** undergo a two-electron oxidation process similar to TTFV precursor **1** upon electrochemical oxidation. Given the already known conformational switching behavior of TTFV **1** taking place in electrochemical redox reaction,[5] it is reasonably to believe that the conformations of the two molecular tweezers **3** and **5** should be electrochemically controllable as proposed in Scheme 1.

In summary, two new TTFV-hinged molecular tweezers with AQ or TTFAQ as the side groups were synthesized via sequential Sonogashira and HWE reactions. Electrochemical and spectroscopic analyses revealed significant electronic communications between the central TTFV and the side groups (AQ or TTFAQ) through π-conjugation. In both of the molecular tweezers, the TTFV molecular hinge undergoes a simultaneous two-electron transfer to form stable dication. This process features chemical reversibility, which suggests usefulness in the preparation of molecular switching devices. We are currently investigating the supramolecular guest–host chemistry of this type of TTFV molecular tweezers, and further results will be disclosed in due course.

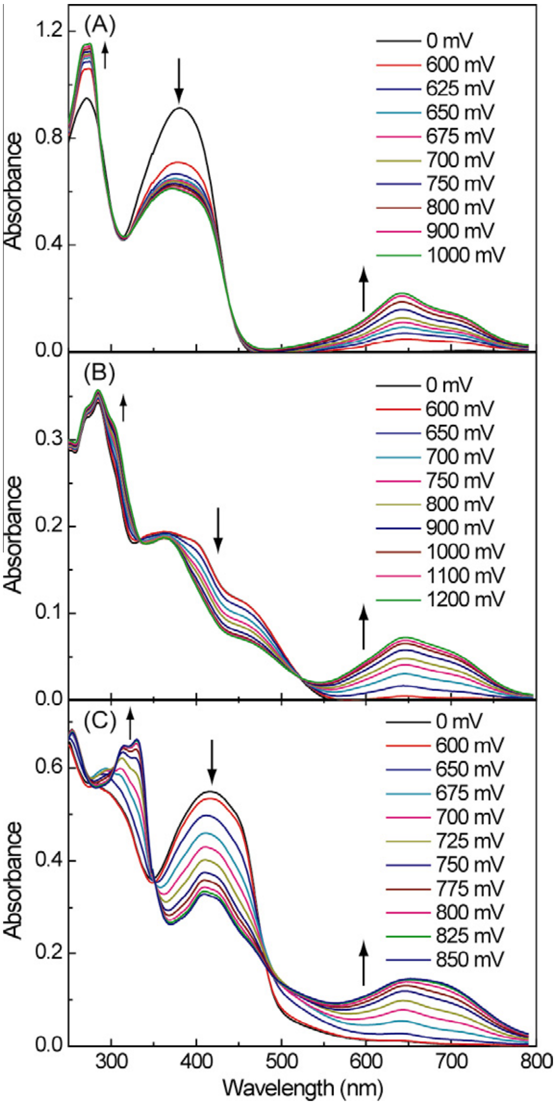


Figure 3. UV–vis spectral changes with increasing applied potential steps during electrolysis. Experimental conditions: Bu_4NBF_4 (0.1 M) as supporting electrolyte; CH_2Cl_2 as solvent; Pt mesh as working electrode; Pt wire as counter electrode; Ag/AgCl as reference.

Acknowledgments

The authors thank NSERC, CFI, and Memorial University of Newfoundland for funding support.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.10.032.

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10. (a) Spectroscopic data for **3**: a red solid, mp >290 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42 (s, 2H), 8.35–8.32 (m, 4H), 8.29 (d, $J = 8.1$ Hz, 2H), 7.68–7.62 (m, 4H), 7.80 (dd, $J = 8.1, 0.9$ Hz, 2H), 7.84–7.79 (m, 4H), 7.43–7.55 (m, 8H), 2.46–2.36 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.9, 182.7, 139.2, 137.7, 136.6, 134.5, 134.4, 133.8, 133.7, 133.6, 132.51, 132.46, 130.4, 129.9, 127.61, 127.55, 127.52, 126.6, 125.6, 123.4, 120.4, 94.8, 89.1, 19.2, 19.1; FTIR (neat): 2919, 2854, 2209, 1672, 1588, 1516, 1477, 1323, 1282, 974, 929, 850 cm^{-1}; MALDI-TOF MS (+eV) *m/z* calcd for $C_{56}H_{34}O_4S_8$ 1026.0223, found 1026.0163 (M^+). (b) Spectroscopic data for **5**: an orange solid, mp 230–231 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, $J = 1.3$ Hz, 2H), 7.57–7.54 (m, 4H), 7.52 (d, $J = 8.1$ Hz, 2H), 7.52–7.48 (m, 4H), 7.45–7.43 (dd, $J = 8.1, 1.3$ Hz, 2H), 7.43–7.38 (m, 4H), 7.32–7.30 (m, 4H), 2.45 (s, 6H), 2.42–2.38 (m, 30H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2, 137.0, 135.0, 134.69, 134.67, 133.0, 133.6, 132.23, 132.22, 129.7, 129.1, 128.8, 128.4, 126.7, 126.6, 126.5, 126.43, 126.36, 126.2, 126.0, 125.7, 125.63, 125.57, 125.4, 123.8, 123.4, 123.0, 121.5, 121.4, 90.48, 90.45, 19.3, 19.2, 19.1; FTIR (neat): 2919, 2854, 1672, 1530, 1492, 1418, 1310, 1215, 964, 891, 837 cm^{-1}; MALDI-TOF MS (+eV) *m/z* calcd for $C_{76}H_{58}S_{24}$ 1737.7836, found 1737.7771 (M^+).