



TTFAQ-cored D/A ensembles: synthesis, electronic properties, and redox responses to transition metal ions

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ABSTRACT

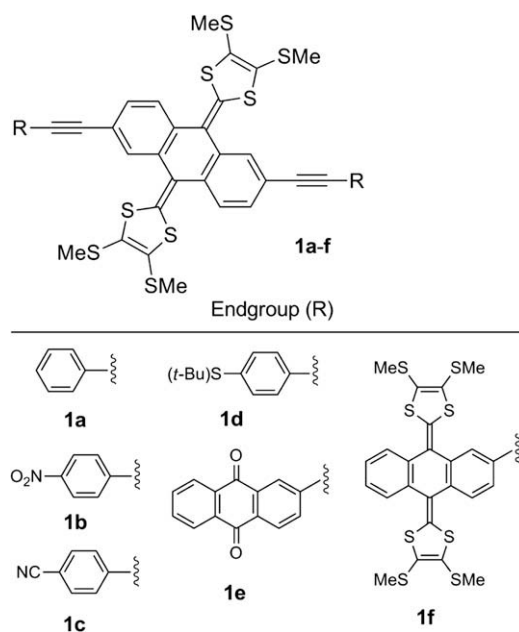
Two anthraquinone-type π -extended tetrathiafulvalene (TTFAQ)-cored D/A triads were synthesized and characterized by UV–vis absorption and cyclic voltammetric analyses. Electronic substituent effects were unraveled by making a comparison with analogous TTFAQ derivatives previously reported. Electrochemical titrations of the two TTFAQ D/A triads with selected transition metal cations (Ag^+ and Cu^{2+}) were examined by cyclic voltammetry, and the results suggest potential application of such TTFAQ derivatives as electrochemical sensors for transition metal ions.

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π -Extended analogues of tetrathiafulvalenes (exTTFs) have received considerable attention in the current TTF chemistry owing to their wide ranging application as redox-active building blocks for molecular-based electronic and optoelectronic devices and materials.¹ In particular, the exTTFs bearing an anthraquinone (AQ)-type π -spacer, generally referred to as TTFAQs, present a class of robust two-electron donors frequently employed in the construction of complex donor/acceptor (D/A) molecular arrays with other electroactive or chromophoric groups.^{1b,2–8}

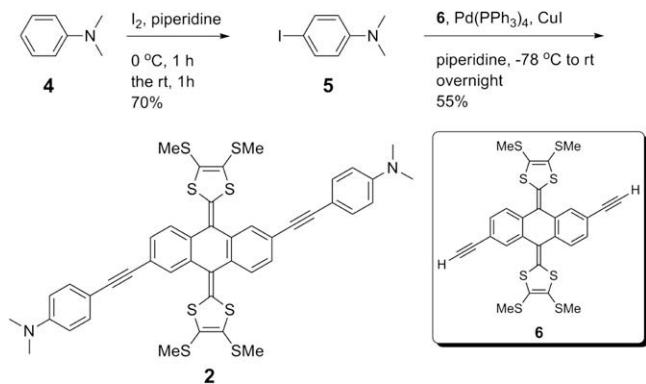
Our group has recently developed a 2,6-dialkynylation strategy that allows for generating various π -extended TTFAQ derivatives (e.g., **1a–f**, Scheme 1) in a facile and modular manner.^{7c,d,9} The acetylenic π -bridge in these compounds has been found to effectively mediate the electronic interactions between TTFAQ and different endgroups, hence enabling electronic and redox properties to be flexibly modulated and finely tuned. This feature could be advantageous in constructing functional molecular devices operated or controlled by electrochemical stimuli or signals; particularly, in the field of electrochemical sensing and molecular recognition.¹⁰ Indeed, molecule systems consist of a receptor (binding) and a reporter (signaling) units have become a motif widely employed in the design of chemosensors. For an efficient chemosensor, the recognition of particular analytes, such as cations, anions, and neutral compounds, is achieved by selective complexation with the receptor unit, while the binding events result in

detectable photophysical or electrochemical responses at the reporter moiety.^{10a,b}



Scheme 1. TTFAQ-cored D/A ensembles previously synthesized via the 2,-dialkynylation strategy.

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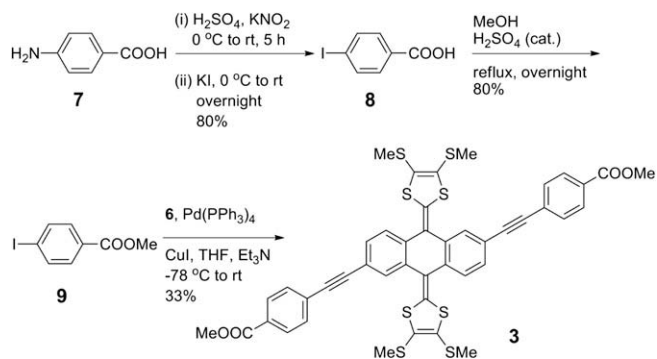


Scheme 2. Synthesis of amino-terminated TTFAQ derivative **2**.

In the literature, a plethora of molecular systems capable of electrochemically sensing and recognizing specific chemical species or ions has been prepared based on redox-active organic electrophores, such as ferrocene, metallocenes, and TTF derivatives.^{10,11} In this study, we investigated the potential of TTFAQ as electrochemical reporter for the detection of transition metal ions. The swift and efficient detection of various transition metal cations is of great importance in analytical and environmental chemistry. Organic functional groups containing heteroatoms such as amino and carboxyl groups can strongly interact with transition metal cations, and the resulting Lewis acid–base complexes usually exhibit considerably altered electronic nature in comparison with the free ligands. Upon this consideration, two new TTFAQ-cored D/A ensembles (**2** and **3**), in which the terminal functionalities are amino or carboxylic ester groups, were prepared and characterized. These two TTFAQ derivatives not only add new members to the TTFAQ-cored D/A triad family but were also expected to serve new TTFAQ-based redox-active ligands for the detection of transition metal ions.

The synthesis of TTFAQ-cored D–D–D type triad **2** was implemented through a divergent approach as described in Scheme 2. Iodination of *N,N*-dimethylaniline (**4**) with molecular iodine in the presence of piperidine afforded *para*-iodo-*N,N*-dimethylaniline **5** in a decent yield. Compound **5** was then doubly cross-coupled with 2,6-diethynyl-TTFAQ **6** under the catalysis of Pd/Cu to give product **2** in 55% yield.¹² It is worth noting that initial efforts to perform the Sonogashira reaction in a mixture solvent (THF/Et₃N, 1:1), which is a common protocol successfully used for a wide range of Sonogashira couplings, failed unexpectedly. After a number of trials, the use of pure piperidine in lieu of THF/Et₃N was found to be the best condition for coupling electron-rich phenyliodide with ethynylated TTFAQ **6**.

The synthesis of A–D–A type TTFAQ-core triad **3** was carried out adopting a similar cross-coupling strategy to that used for **2**. As



Scheme 3. Synthesis of carboxylic ester-terminated TTFAQ derivative **3**.

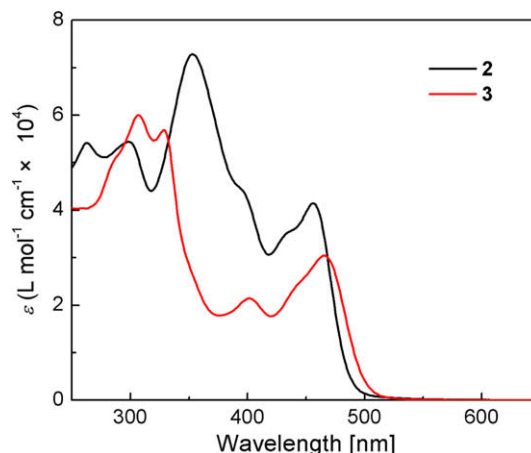


Figure 1. UV–vis absorption spectra of compounds **2** and **3** measured in CHCl₃ at room temperature.

shown in Scheme 3, *para*-aminobenzoic acid (**7**) was converted into iodide **8** via a Sandmeyer reaction. Compound **8** underwent a Fischer esterification reaction in refluxing MeOH and the presence of a catalytic amount of H₂SO₄ to give methyl *para*-iodobenzoate (**9**) in 80% yield. Cross-coupling of compound **8** and TTFAQ **6** under typical Sonogashira conditions then afforded the desired product **3** in a moderate yield of 33%.¹³

The electronic properties of the two TTFAQ derivatives, **2** and **3**, were investigated by UV–vis absorption spectroscopy. Figure 1 shows the absorption spectra of **2** and **3** measured in CHCl₃, and detailed spectroscopic and electrochemical data are summarized in Table 1.

From the UV–vis spectroscopic analysis, the lowest-energy absorption band of compound **2** at 453 nm is found to blueshift by 7 nm relative to that of **3** (460 nm). This observation signifies a narrower HOMO–LUMO gap in **3** as a result of the electron push–pull effects^{7c,d} among the electron-donating TTFAQ moiety and two electron-withdrawing carboxylic ester endgroups. The amino (donor) attached TTFAQ **2** shows molar extinction coefficients (ϵ) that are considerably greater than those of carboxylic ester (acceptor) endcapped TTFAQ **3** in the low-energy region. To further probe the D/A-substituent effects on the electronic spectroscopic behavior, the UV–vis spectral data of **2** and **3** were compared with analogous D/A-substituted TTFAQs **1a–d**, and the details are listed in Table 2.

A clear trend can be established from Table 2 that the lowest-energy absorption peak (λ_{max}) that corresponds to HOMO to LUMO transition energy is redshifted as the substituent increases with acceptor strength (σ_{para}).¹⁴ Conversely, the electron-donating substituent causes a blueshift of the λ_{max} value in comparison with the unsubstituted TTFAQ **1a**. Of note is that the λ_{max} of **1d** is noticeably redshifted by 3 nm relative to **1a**. This result indicates that the

Table 1
UV–vis spectroscopic and electrochemical data of **2** and **3**

Entry	λ_{abs} (nm)	ϵ (L mol ⁻¹ cm ⁻¹)	E_{pa} (V)	E_{pc} (V)
2	453	4.1×10^4	+0.56	–
	391 (sh)	4.5×10^4	+0.92	
	350	7.2×10^4		
	295	5.4×10^4		
	259	5.3×10^4		
3	460	2.9×10^4	+0.61	+0.47
	396	2.1×10^4		
	325	5.6×10^4		
	305	6.0×10^4		

Table 2
Substituent effects on the UV–vis absorption behavior of D/A-substituted TTFAQs **1–3**

Entry	Substituent	λ_{\max}^a (nm)	ϵ (L mol ⁻¹ cm ⁻¹)	$\Delta\lambda_{\max}^b$ (nm)	σ_{para}^c
1a	H	458	2.7×10^4	0	0
1b	NO ₂	470	2.2×10^4	+12	+0.81
1c	CN	470	1.9×10^4	+12	+0.70
1d	S(<i>t</i> -Bu)	461	2.6×10^4	+3	–
2	NMe ₂	453	4.1×10^4	–5	–0.83
3	COOCH ₃	460	2.9×10^4	+2	+0.45

^a Wavelength of the lowest-energy absorption peak.

^b Shift of λ_{\max} relative to unsubstituted TTFAQ **1a**.

^c Substituent constant taken from Ref. 14.

S(*t*-Bu) group in **1d** should be deemed as weakly electron-withdrawing as a result of its relatively stronger inductive effect which prevails over its resonance (electron-donating) effect.

The redox properties of TTFAQs **2** and **3** as well as their electrochemical responses to selected transition metal ions (Ag⁺ and Cu²⁺) were investigated by cyclic voltammetry. In the cyclic voltammogram of **2** (see Fig. S-5 in Supplementary data), two irreversible anodic peaks were clearly seen at +0.56 and +0.92 V. The first peak can be assigned to a simultaneous two-electron oxidation of the central TTFAQ core,^{7c} while the second peak is due to the oxidation of the terminal amino groups. The irreversible redox behavior is in stark contrast to other TTFAQ analogues, wherein oxidation of the TTFAQ moiety usually gives rise to a quasi-reversible redox wave pair. A plausible explanation for the irreversibility is that swift chemical reaction(s) took place after the oxidation of the amino groups. In the cyclic voltammogram of **3** (see Fig. S-5 in Supple-

mentary data), a quasi-reversible wave pair is discernible at +0.61 (anodic) and +0.47 V (cathodic), respectively, which is characteristic of TTFAQ. The anodic potential is higher than that of **2**, which testifies to the electron-withdrawing effect of the carboxylic ester groups.

Conceivably, the amino groups and carboxyl groups of **2** and **3** are Lewis bases that could function as ligands to coordinate with transition metal ions. If such complexation occurs, the electronic nature of the substituent should be considerably modified. In principle, the TTFAQ core in the resulting complexes should be more electron-deficient in comparison with their neutral states, hence leading to anodically shifted oxidation potentials.

In the experiments, aliquots of AgOTf or Cu(OTf)₂ were titrated to the solutions of TTFAQ derivatives **2** and **3**, and the titration processes were monitored by cyclic voltammetry. Worth noting is that upon metal cation titrations (Ag⁺ and Cu²⁺), both the solutions of **2** and **3** changed from orange into dark brown color, which is suggestive of significant metal–ligand complexation. The titration results shown in Figure 2, surprisingly, appear to be more complex than expected. In Figure 2B and D, the increasing addition of Cu²⁺ to **2** considerably reduced the current intensity of the second anodic peak ($E_{\text{pa}} = +0.92$ V), which corresponds to the oxidation of amino moieties. This observation confirms that the amino groups of **2** are the active binding sites for complexation with Cu²⁺ cation. The addition of Cu²⁺ to **3** also reduced appreciably the current intensity of the anodic peak of TTFAQ ($E_{\text{pa}} = +0.61$ V), substantiating the complexation between **3** and Cu²⁺. Besides, as the titration progressed, the redox wave due to Cu²⁺ at +1.16 V was observed to shift cathodically. In contrast to the Cu²⁺ titration data, titrations

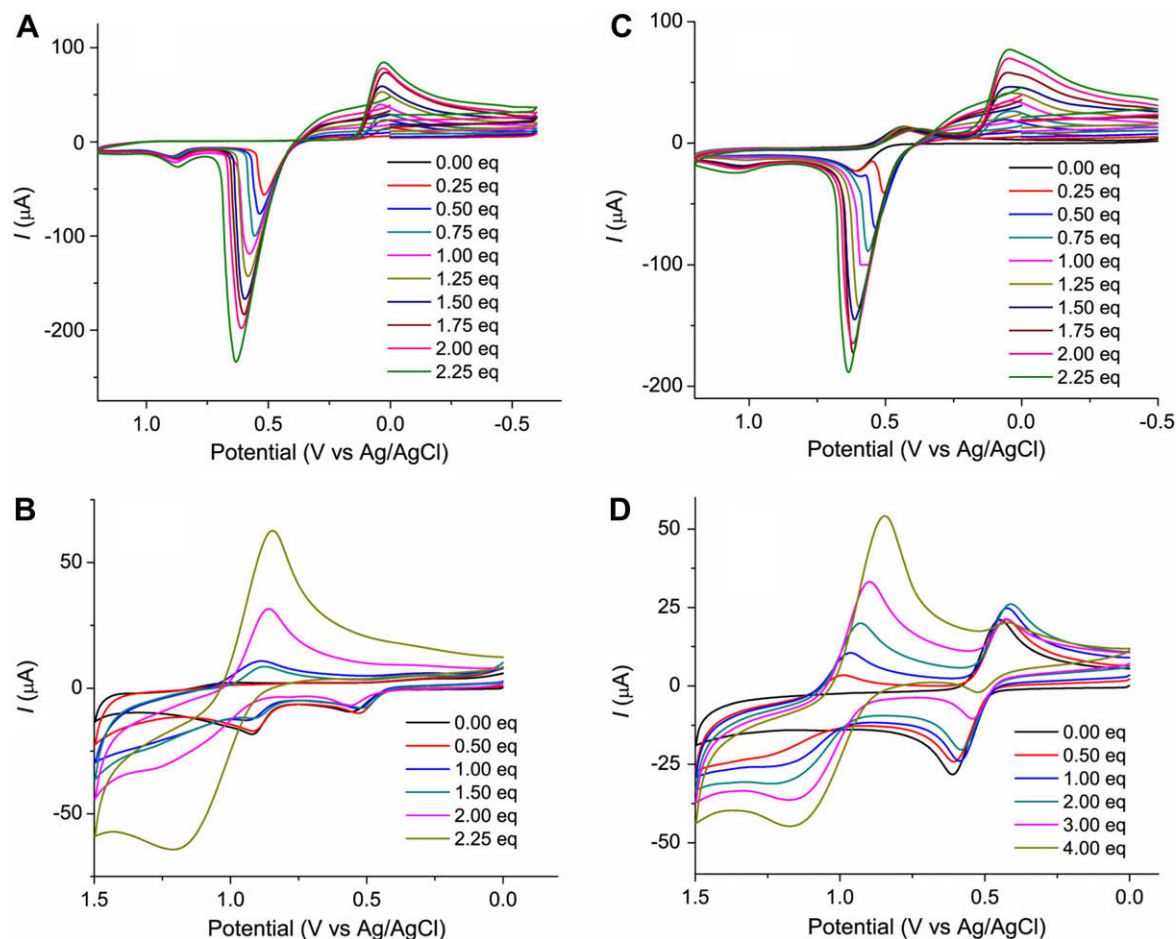


Figure 2. Cyclic voltammetric titrations of (A) **2** (1.0 μM) and AgOTf; (B) **2** (1.0 μM) and Cu(OTf)₂; (C) **3** (1.0 μM) and AgOTf; (D) **3** (1.0 μM) and Cu(OTf)₂. Electrolyte: Bu₄NBF₄ (0.1 M); solvent: CH₂Cl₂/CH₃CN (4:1); working electrode: glassy carbon; counter electrode: Pt; reference electrode: Ag/AgCl.

of Ag⁺ to **2** and **3**, respectively, did not cause any significant changes in the redox features of TTFAQ, thus ruling out the possibility of significant interactions between Ag⁺ and S atoms in **3**. On the other hand, the anodic peak at ca. +0.58 V due to Ag⁺ was observed to move anodically with increasing titration, the exact reason for such shift is unclear and awaits further exploration.

In conclusion, two new D/A-substituted TTFAQ derivatives **2** and **3** were prepared and added to the family of TTFAQ-cored D/A triads. Availability of these compounds has allowed for a systematic examination of the D/A substitution effects on the electronic spectroscopic properties of TTFAQ through acetylenic conjugation. Electrochemical titration experiments on TTFAQ derivatives **2** and **3** with selected metal ions have demonstrated good sensing selectivity for Cu²⁺ ions. Application of such D/A TTFAQ triads as electrochemical sensors for other transition metal ions (e.g., Pb²⁺, Cd²⁺, Hg²⁺, Zn²⁺, etc.) is under investigation and will be reported in due course.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.03.099.

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- Characterization data for compound 2**: An orange solid. Mp: 250–252 °C; IR (neat): 2918, 2852, 2197, 1609, 1593 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.64 (s, 4H), 7.51 (d, J = 7.9 Hz, 2H), 7.46–7.41 (m, 6H), 6.69 (d, J = 7.9 Hz, 4H), 3.00 (s, 12H), 2.41 (s, 12H); HSQC data see [Supplementary data](#); HRMS (MALDI-TOF, m/z) calcd for C₄₄H₃₈N₂S₈: 850.0801 [M]⁺, found: 850.0869.
- Characterization data for compound 3**: an orange solid. Mp: 135–136 °C; IR (neat): 2948, 2920, 2205, 1724, 1605, 1527 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.04 (d, J = 8.4 Hz, 4H), 7.69 (d, J = 1.3 Hz, 2H), 7.63 (d, J = 8.4 Hz, 4H), 7.55 (d, J = 8.4 Hz, 2H), 7.48 (dd, J = 8.0, 1.5 Hz, 2H), 3.94 (s, 6H), 2.42 (s, 12H); ¹³C NMR (125 MHz, CDCl₃): δ 166.5, 134.8, 134.6, 131.6, 129.8, 129.58, 129.55, 128.2, 127.9, 126.7, 125.8, 125.5, 122.1, 120.7, 92.3, 89.5, 52.5, 19.42, 19.25 (one signal not observed due to coincidental overlap); HRMS (MALDI-TOF, m/z) calcd for C₄₄H₃₂O₄S₈: 880.0066 [M]⁺, found: 880.0057.
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