



Ferrocenyl-triazolyl-tetrathiafulvalene assemblies: synthesis and electrochemical recognition properties

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ABSTRACT

Cu(I)-catalyzed Huisgen–Meldal–Sharpless type dipolar ‘click’ reactions between azido-tetrathiafulvalene derivatives and ethynylferrocene yield the first examples of ferrocenyl-1,2,3-triazolyl-tetrathiafulvalene assemblies (**4a**, **4b**). The electrochemical behavior of **4a** and **4b**, which integrate two distinctive redox probes, has been investigated, and their binding ability for various transition-metal cations has been studied by cyclic voltammetry. The contribution of the triazolyl ring in the guest binding process is illustrated by the specific electrochemical recognition of Zn²⁺ by receptor **4b**.

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Tetrathiafulvalene (TTF) is a well-established reversible two-electron donor and has found a widespread use in supramolecular chemistry.¹ Since the seminal works on the solid-state high electrical conductivity of cation-radical salts and charge-transfer complexes of tetrathiafulvalene,^{2–4} a myriad of TTF derivatives have been synthesized. They have allowed to apply this unit to new horizons, related to studies led in solution, with the ultimate goal to construct redox-switchable systems at the molecular or supramolecular level, as for example sensors for ions or neutral molecules.^{1,5} On the other hand, ferrocene (Fc) undergoes a fast and reversible one-electron oxidation at a readily accessible redox potential and is a very popular electroactive unit, used in various fields of chemistry ranging from ligands for catalytic applications, to conducting materials and supramolecular chemistry.^{6,7}

Due to their respective electrochemical properties, the covalent combination between TTF and Fc appears of strong interest. Such assemblies should lead to multistage redox systems and a first example was designed by Ueno et al. for the generation of charge-transfer complexes at the solid state.⁸ The potentiality of TTF-Ferrocene architectures was reviewed⁹ and a recent extension was proposed by Sarhan et al., who reported an efficient route to π -extended tetrathiafulvalenes incorporating ferrocenes.¹⁰ Consid-

ering their rich electrochemical properties, TTF-Fc derivatives may also be used to develop dual electrochemical recognition sensors, and no example has been depicted in this area so far.

The chemical compatibility of the TTF unit for Cu(I)-catalyzed ‘click’ reaction was recently shown through several examples.^{11–14} We herein report the use of a copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction^{15–18} between TTF-azide and ethynylferrocene to synthesize the first TTF-Fc derivatives linked by 1,2,3-triazoles groups. The cyclic voltammetry studies demonstrate that these two TTF-Fc compounds **4a** and **4b** exhibit distinctive electrochemical responses in the presence of specific transition metal cations.

The synthetic route to target compounds is depicted in Scheme 1. The starting materials **1a** and **1b** were obtained according to the reported procedures.^{19–22} The reaction of **1a** and **1b** with NaN₃ in DMF produced the terminal TTF-azides **2a** (75%) and **2b** (70%),²³ respectively. The final click reaction of ethynylferrocene **3**²⁴ with TTF-azides **2a,b** was carried out in DMF using CuI–NET₃, to give the target ferrocenyl-triazolyl-tetrathiafulvalenes **4a** (54%) and **4b** (41%), respectively.²⁵ The chemical structure of compounds **4a** and **4b** were confirmed by ¹H (¹³C) NMR, FT-IR, mass spectroscopic data, and elemental analysis.

The electrochemical properties of the ferrocenyl-triazolyl-tetrathiafulvalene assemblies **4a** and **4b**, as well as of the parent units TTF(SMe)₄ and ferrocene for comparison, were investigated by cyclic voltammetry (CV) in a dichloromethane–acetonitrile (1/1, v/v) mixture (Fig. 1 and Table 1). As seen from Figure 1, the TTF(SMe)₄

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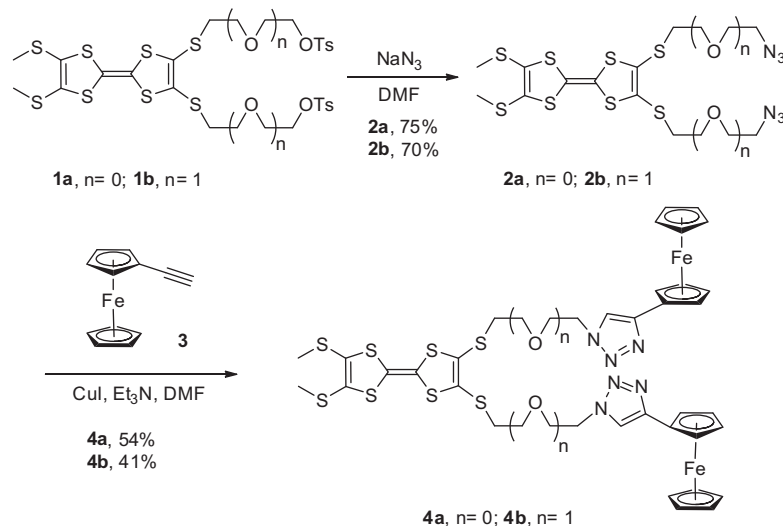
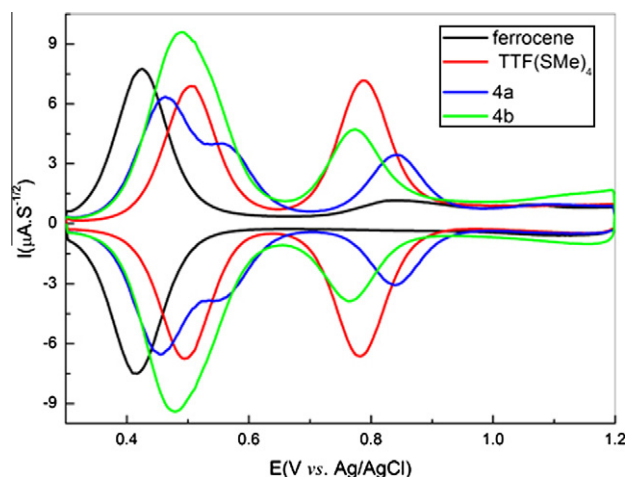
Scheme 1. Synthetic access to **4a,b**.

Figure 1. Deconvoluted CV study of **4a**, **4b**, TTF(SMe)₄, and ferrocene (ca 0.5 mM), CH₂Cl₂/CH₃CN (1:1, V/V), Bu₄NPF₆ (0.2 M), $v=0.1$ V/s, Pt ($\varphi 2 \times 10^{-3}$ m), versus Ag/AgCl.

Table 1

Half-wave potentials measured by cyclic voltammetry (V), solvent: CH₂Cl₂/CH₃CN (1:1, V/V); electrolyte: 0.2 M Bu₄NPF₆; scan rate: 100 mV/s; reference electrode: Ag/AgCl; working electrode: platinum ($\varphi=2 \times 10^{-3}$ m)

Compound	$E_1^{1/2}$	$E_1'^{1/2}$	$E_2'^{1/2}$
Ferrocene	0.421	—	—
TTF(SCH ₃) ₄	—	0.502	0.785
4a	0.459	0.556	0.841
4b	—	0.484	0.771

undergoes two successive reversible one-electron redox processes leading, to cation-radical and dicationic species, respectively, and the ferrocene exhibits a reversible one-electron process corresponding to the ferrocene/ferricenium couple. Both assemblies **4a** and **4b** present two distinctive electrochemical behaviors. The TTF-Fc **4a** shows three successive reversible redox waves with two, one, and one electrons exchanged upon the positive scanning. Both ferrocene units in **4a** are independently oxidized with one electron each, followed by the two one electron oxidation of the TTF unit. The ferrocene/ferricenium couple in **4a** ($E_1^{1/2} = +459$ mV) appears at a more positive potential than in the case of ferrocene

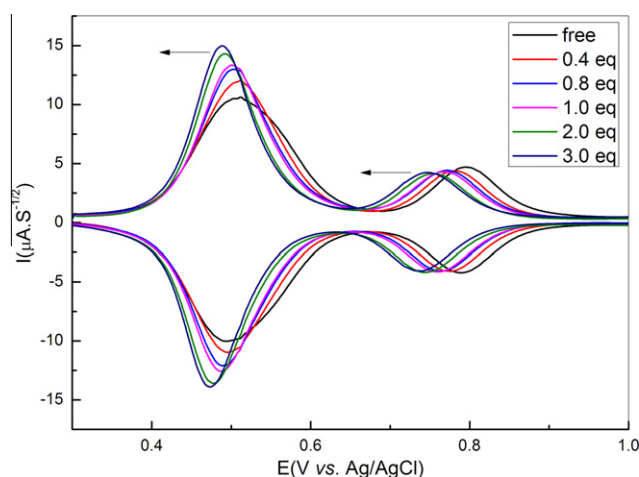


Figure 2. Deconvoluted CV changes for **4b** (0.5 mM) upon addition of ZnClO₄·CH₂Cl₂/CH₃CN (1:1, V/V), Bu₄NPF₆ (0.2 M), $v=0.1$ V/s, Pt ($\varphi 2 \times 10^{-3}$ m), versus Ag/AgCl.

($E_1^{1/2} = +421$ mV), which accounts for the electron-withdrawing ability of the triazolyl group directly connected to the ferrocene unit in **4a**. The second ($E_1'^{1/2} = +0.556$ mV) and third ($E_2'^{1/2} = +841$ mV) oxidation peaks, related to the TTF unit, are also positively shifted compared to that of the parent TTF(SMe)₄ ($E_1^{1/2} = +484$ mV, $E_2'^{1/2} = +771$ mV). In this case, the anodic shift of both redox potentials is assigned to both the electron-withdrawing character of the triazolyl groups, as well as to the positively charged ferricenium units which is now formed in the proximity of the TTF backbone. It is worth noting that the TTF-Fc assembly **4b** which integrates a longer linker between TTF and ferrocene units, shows only two reversible redox waves, corresponding to three and one electrons exchanged, respectively. This observation accounts to the merging of both ferrocene oxidations with the first TTF oxidation and suggests lower interactions between TTF and ferrocene units, which are assignable to the longer linker in **4b**. The second redox process ($E_2'^{1/2}$) corresponds to the one-electron oxidation to the TTF²⁺ state and is located at a closely similar potential as for parent TTF(SMe)₄, confirming a lower through space interaction with ferrocene units in the case of **4b**.

The recognition properties of ferrocenyl-triazolyl-tetra-thiafulvalene assemblies **4a** and **4b** for transition-metal cations

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