

Synthesis and electronic properties of alkyne–TTFAQ based molecular wires

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Abstract—We herein describe the first synthesis of a series of π -extend tetrathiafulvalene and alkyne based conjugated molecular wires. Electronic properties of these compounds were characterized by cyclic voltammetry, UV–vis absorption, and fluorescence spectroscopy.

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Tetrathiafulvalenes (TTFs) are renowned π -electron donors and are very useful as organic charge-transfer materials.¹ Ever since the first discovery of TTF in the early 1970s, considerable attention has been devoted to expanding the family of TTF derivatives.² An important strategy to create new TTF structures is to extend the conjugation path between the two dithiole rings of a TTF molecule, resulting in the so-called π -extended TTFs (exTTFs).³ Of numerous reported exTTFs, 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives⁴ (henceforth referred to as TTFAQs) show the most significantly enhanced electron donor ability. This is because of the strong tendency to form planar, aromatic oxidized states from highly distorted nonaromatic ground states by sequentially releasing two electrons. Moreover, the number of redox states accessible within TTFAQ is increased compared to TTF. Owing to these properties, TTFAQs have been widely applied as key active components in a plethora of molecule-based electronic and optoelectronic materials.

One way to take advantage of the outstanding electroactivities of TTFAQs in unimolecular electronic devices is to combine them with various electroactive structures, for example, molecular wires and π -electron acceptors. Along this line, copious TTFAQ-based assemblies have emerged over the past decades, in which the exTTF units are covalently bonded to other structures primarily

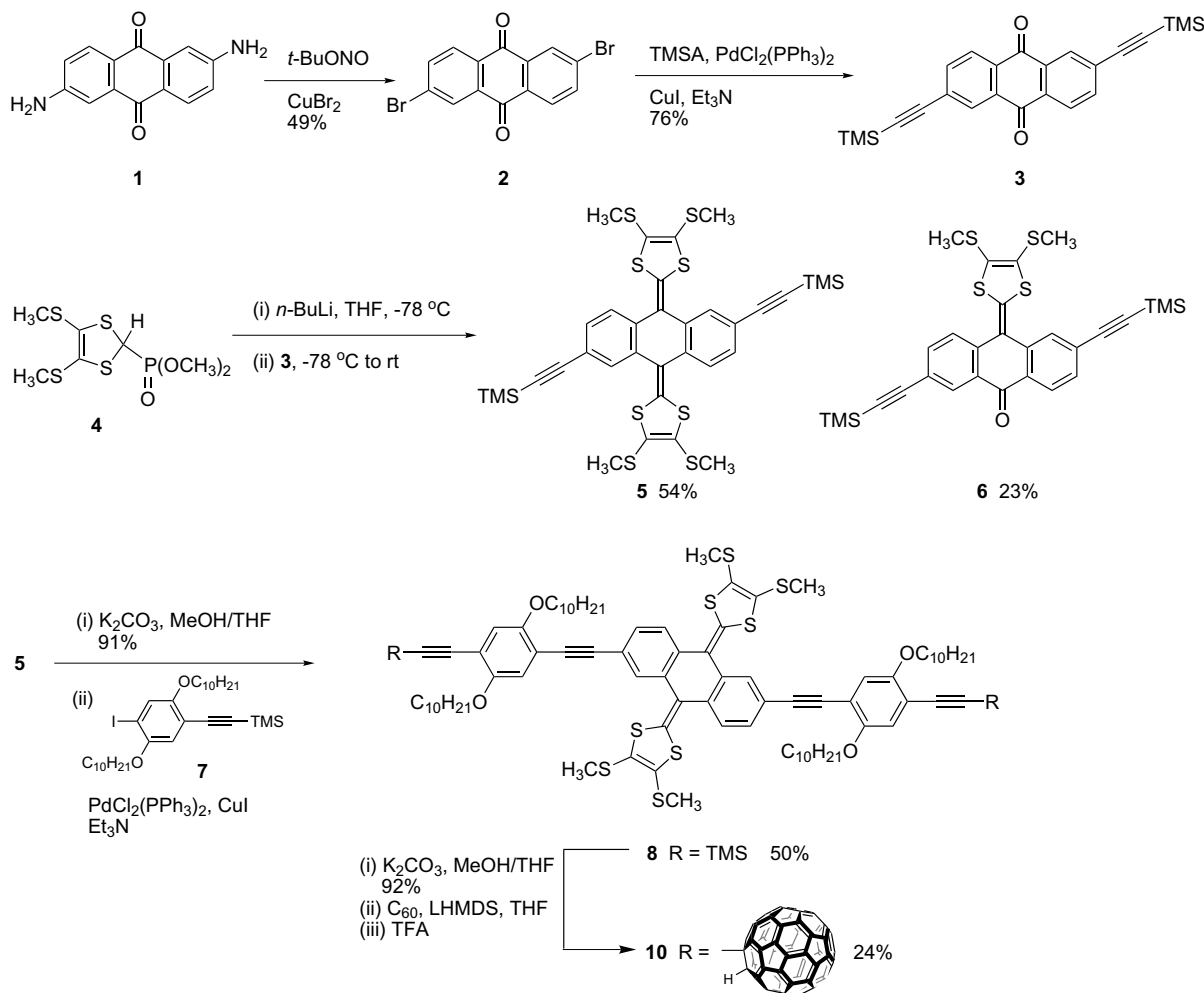
through ester,⁵ vinylene,⁶ and ether groups.⁷ Surprisingly, to the best of our knowledge, acetylenic group has never been investigated as possible linkage in TTFAQ derivatives, despite the fact that acetylenic scaffolds⁸ have been well recognized as powerful building blocks for a variety of π -conjugated molecular architectures, even including some alkyne-extended TTFs.⁹ To address this issue, we herein report the first synthesis and characterization of a series of alkyne–TTFAQ based molecular wires.

In order to achieve full conjugation along the entire molecular framework, we designed 2,6-dialkynyl substituted TTFAQ **5** (see Scheme 1) as a key central unit for the molecular wire. It is worth noting that the prominent topological characteristics of **5** lies in the increase of conjugation dimensionality along the anthracene–acetylene direction which is orthogonal to the dithiole–quinone conjugation path. Moreover, in the ground state, the 2,6-dialkynyl units are *cross-conjugated* to each other, whereas in the dicationic oxidation state the two alkynyl units become *conjugated* due to the formation of the anthracene-type structure. As such, compound **5** constitutes a versatile synthetic platform for generating new exTTF containing molecular wires or switches.

The synthesis of **5** is outlined in Scheme 1. 2,6-Diaminoanthraquinone (**1**) was first converted into dibromide **2** through a Sandmeyer reaction.¹⁰ Compound **2** underwent Sonogashira coupling with trimethylsilylacetylene (TMSA) to afford **3**. Wittig–Horner reaction of **3** with compound **4**¹¹ in the presence of *n*-BuLi yielded compound **5**. In this reaction, however, a significant amount

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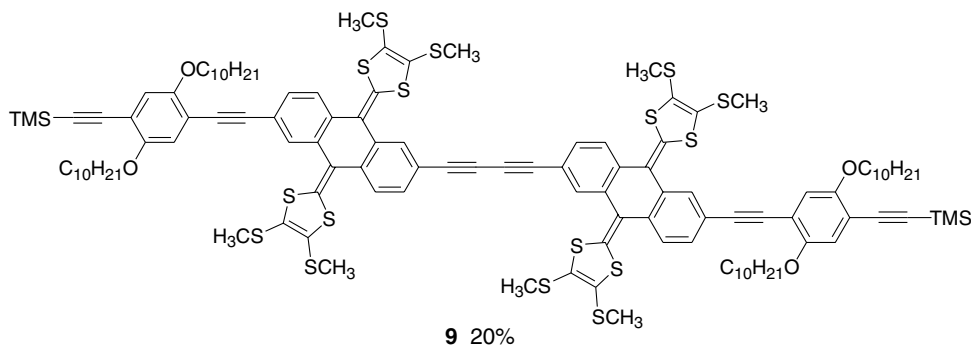
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Scheme 1. Synthesis of alkyne–TTFAQ molecular wires.

of byproduct **6** was also formed, indicating a relatively low reactivity of diketone **3** to the Wittig–Horner olefination. Compound **5** then allowed us to readily access the desired TTFAQ centered molecular wires. Because of

ingly, in this reaction a TTFAQ–arylacetylene dimer **9** was obtained as well. The formation of **9** is ascribed to the homocoupling reaction taking place immediately after the cross-coupling of desilylated **5** with 1 equiv of **7**.



the moderate solubility of **5** in common organic solvents, long alkoxy chain-attached arylacetylene iodide **7**¹² was chosen as a solubility enhancing conjugative arm for molecular chain elongation. As illustrated in **Scheme 1**, compound **5** was desilylated with K_2CO_3 and then cross coupled with **7** under Sonogashira coupling conditions to give molecular wire **8**. Interest-

As excellent electron donors, TTFAQs have been widely employed in the preparation of artificial photosynthetic systems, where fullerene C_{60} is commonly adopted as the counterpart electron acceptor. A dumbbell shaped C_{60} –exTTF– C_{60} triad was recently synthesized by Martín and co-workers.^{13a} Photophysical study revealed that the triad could lead to stable charge-separated (C–S)

species with a rather long lifetime (ca. 600 ns in benzonitrile) upon photoexcitation. In the molecule, however, the exTTF unit and C₆₀ groups are bridged through nonconjugated structures. Given that electronic coupling is a determining factor to photodeactivation pathways in various donor–acceptor ensembles, it is anticipated that inserting fully conjugated bridges between C₆₀ and exTTF units should facilitate the formation of C-S states and, as a result, give rise to improved photophysical outcomes. In this context, we have synthesized a new type of C₆₀–TTFAQ–C₆₀ triad **10** using molecular wire **8** as the bridging unit. It should be noted that in **10**, each of the two C₆₀ groups is linked to the conjugated TTFAQ–aryleneacetylene backbone via only one sp³ carbon.

The synthesis of triad **10** was undertaken via an in situ ethynylation protocol.¹² Alkyne–TTFAQ wire **8** was desilylated with K₂CO₃ to yield the corresponding terminal alkyne species, which was subsequently reacted with excess C₆₀ in the presence of a strong base, lithium hexamethyldisilazide (LHMDS). After quenching the reaction with trifluoroacetic acid (TFA), compound **10** was obtained in 25% yield. Triad **10** is relatively stable at room temperature and has decent solubility in organic solvents, which allow its structure to be fully elucidated by IR, NMR, and MS.

Electrochemical redox properties of compounds **5–6** and **8–10** were characterized by cyclic voltammetry (CV) experiments. The obtained data are summarized in Table 1. The cyclic voltammograms of all the five compounds exhibit amphoteric redox behavior (see Table 1). Compounds **5** and **8–10** all show a similar reversible or quasireversible oxidation wave pair in the positive potential region ranging from +0.44 to +0.54 V. This redox wave is presumably due to the two-electron oxidation process occurring at the TTFAQ unit. It is also noticeable in **5** and **8–10** that the half wave potential of the oxidation wave ($E_{1/2ox}$) shifts to the positive potential direction as the molecular size increases. This trend is in line with the assumption that more energy is required to achieve the planar oxidation state from the highly distorted ground state as the size of substituents on TTFAQ increases. For compound **6**, however, the $E_{1/2ox}$ value (+0.98 V) is much greater than the others, because of the weaker electron donor ability of the

mono-dithiole ring structure than TTFAQs. In the negative potential region, molecular wires **5** and **8** show noticeable irreversible reduction processes peaking at –1.84 and –1.79 V, respectively. In the cyclic voltammogram of C₆₀–TTFAQ–C₆₀ triad **10**, the first reduction process is irreversible, while the second and third reductions are reversible. No peak splitting was observed on the C₆₀ reduction waves, indicating that the two C₆₀ fragments in compound **10** have no significant mutual interactions. This result is in accord with the cyclic voltammetric data for other reported dumbbell shaped C₆₀–oligomer–C₆₀ systems.^{12,13} Moreover, it is worth noting that, according to the electrochemical data obtained, a narrow HOMO–LUMO gap of 1.14 eV was characterized for C₆₀–TTFAQ–C₆₀ triad **10**. Such a small bandgap could render this molecule useful in the fields such as organic semiconducting and nonlinear optical devices.

Electronic absorption and emission properties of compounds **5**, **6**, and **8–10** were investigated by UV–vis and fluorescence spectroscopy. A summary of spectroscopic data and bandgap (E_g) values calculated from UV–vis and electrochemical data are given in Table 2.

In the UV–vis spectra of **5**, **8**, and **9**,¹⁴ the lowest-energy absorption wavelength (λ_{max}), which is assigned to $\pi \rightarrow \pi^*$ transition, redshifts from 456 to 468 nm with increasing conjugation length along the alkyne direction. However, the degree of redshift (by ca. 12 nm) is not as appreciable as in other linearly conjugated systems, because of the nonplanar TTFAQ core in the ground state. Interestingly, triad **10** has a comparable λ_{max} value (469 nm) to that of **9** (468 nm), albeit its π -conjugation backbone is much shorter than **9**. This result suggests electronic interactions take place between C₆₀ and the conjugated wire. In addition, a weak absorption band centered at 701 nm is observable in the absorption spectrum of **10**, which is assigned to the characteristic absorption of functionalized C₆₀. Compound **6** exhibits a greatly redshifted λ_{max} value (495 nm) compared with others due to the push-and-pull effect between the donor (dithiole) and acceptor (ketone) groups in the molecule.

Fluorescence spectra of compounds **5**, **6**, and **8–10**¹⁴ are given in Table 2 and Figure 1. In the fluorescence

Table 1. Results of cyclic voltammetry for **5**, **6**, and **8–10**^a

Entry	$E_{1/2ox}$ (V)	$E_{1/2red1}$ (V)	$E_{1/2red2}$ (V)	$E_{1/2red3}$ (V)	$E_{1/2red4}$ (V)
5 ^c	+0.44	–1.84 ^b			
6 ^c	+0.98	–1.21	–1.48	–1.93 ^b	
8 ^c	+0.45	–1.79 ^b			
9 ^c	+0.46	–1.64 ^c			
10 ^d	+0.54	–0.60 ^b	–0.92	–1.32	–1.92

^a Cyclic voltammograms were recorded in Bu₄NBF₄ (0.1 M) solution as the supporting electrolyte. Glassy carbon as the working electrode and platinum wire as the counter electrode. Potentials are given in volts versus a Ag/AgCl reference electrode. Scan rate: 100 mV s^{–1}. For chemically reversible processes, half wave potentials ($E_{1/2}$) are calculated as averages of oxidation and reduction peak potentials.

^b For irreversible processes, oxidation or reduction peak potentials are reported as $E_{1/2}$.

^c Solvent: CH₂Cl₂/CH₃CN (4:1).

^d Solvent: *o*-dichlorobenzene/CH₃CN (4:1).

^e Not clearly observed.

Table 2. Summary of spectroscopic data and HOMO–LUMO gaps for **5**, **6**, and **8–10**

Entry	Abs. λ_{\max} (nm)	Em. λ_{\max} (nm)	$E_g(1)^a$ (eV)	$E_g(2)^b$ (eV)
5	456, 388, 294(sh)	501	2.53	2.28
6	495, 382, 324(sh)	629	2.19	2.19
8	465, 367, 301	517, 420	2.48	2.24
9	468, 408(sh), 364	517, 458, 437	2.43	2.10
10	701(C ₆₀), 469, 435, 367, 311(sh)	709, 492	1.74	1.14

^a Optical bandgap calculated by the absorption wavelength at the cross point of a tangential line passing through the turning point of the lowest-energy absorption peak and the x -axis of the UV–vis spectrum.

^b Bandgap calculated based on CV results. $E_g(2) = E_{1/2ox} - E_{1/2red1}$.

spectra, a redshift trend similar to that in the UV–vis data is observed; the lowest-energy emission band, assigned to the $S_1 \rightarrow S_0$ transition, redshifts slightly by ca. 16 nm from **5** (501 nm) to **8** and **9** (517 nm), while the λ_{\max} of **6** redshifts dramatically to 629 nm. In the spectrum of **9**, two additional emission peaks at 458 and 437 nm are discernible, presumably arising from transitions from higher-lying excited states (S_2 and S_3) to the ground state (S_0). In contrast to others, the spectrum of **10** shows substantially quenched emission features corresponding to the conjugated wire structure. The quenching effect implies that rapid intramolecular energy and/or electron transfer processes compete strongly with fluorescence emission in photodeactivation. In addition, a weak emission at ca. 709 nm is distinctly observed in the spectrum of **10**, which is assigned to the $0^* \rightarrow 0$ transition of triplet-state C₆₀.¹⁵ Compared with the UV–vis spectrum of **10**, the Stokes shift is equal to 161 cm^{-1} , which signifies an extremely small total reorganization energy (λ_t) of the C₆₀ cage.

In summary, the synthesis of TTFAQ–alkyne molecular wires offers a new approach for preparing novel exTTF based conjugated structures. Electrochemical studies show that these molecular wires maintain the remarkable electron donor ability of TTFAQ. Electronic absorption and emission spectroscopic analyses indicate that the conjugated acetylenic bridge can facilitate electronic interactions between TTFAQ and other electroactive units. The significantly quenched emission of C₆₀–TTFAQ–C₆₀ triad **10** suggests interesting photophysical properties, which likely involve intramolecular energy and electron transfers. Work is currently in progress to investigate the detailed photophysical dynamics

of **10** with time-resolved fluorescence spectroscopy and nanosecond pulsed laser flash photolysis experiments. Further results will be reported elsewhere.

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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.2006.05.090.

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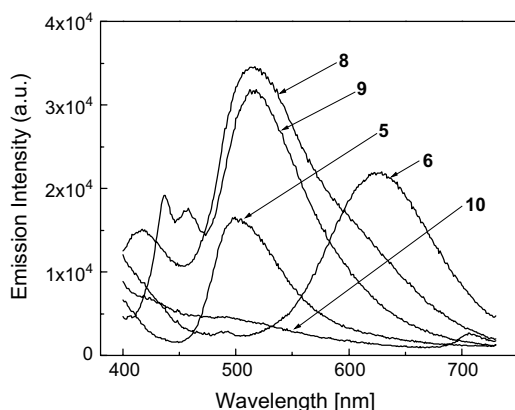


Figure 1. Fluorescence spectra of **5–6** and **8–10** ($\lambda_{\text{ex}} = 380 \text{ nm}$).

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