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Molecular Wires Based on Thienylethynylene: Synthesis, Photophysical Properties, and Excited-State Lifetime

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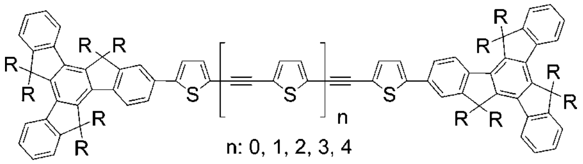
ABSTRACT



A series of π-conjugated molecular wires based on thienylethynylene units have been developed to understand the effect of the molecular structures on their photophysical properties. The investigation of their photophysical properties indicates that the formation of aggregates at the ground state is effectively suppressed by the incorporation of truxene units. The excited-state lifetimes are observed to be biexponential for these molecular wires.

π-Conjugated materials have been extensively investigated due to their applications in a wide range of optoelectronic devices. Such conjugated systems provide an extraordinary channel to transport electronic excitations to segments with the greatest effective conjugation length.[1] Progress in the study of molecular devices through single molecular wires over the past decade has been phenomenal.[2] Synthesizing functional molecular wires with different effective conjugation lengths no doubt permits easier and more reliable fabrication and is also of fundamental importance.

Molecular wires based on rodlike aryleneethynylene backbones are of considerable current interest as optoelectronic materials and as model compounds for structural related polymers.[3,4] Oligo(thienylethynylene)s (OTEs) have attracted considerable interest due to their rigid geometry and ability to effectively transfer energy over long distances.[4] The incorporation of triple bonds in linear OTEs has been demonstrated and investigated for their applications in electronic devices as "molecular wires".[5] In this paper, we present an efficient preparation of a family of molecular wires connecting two truxene moieties through OTE units of different conjugation lengths, **Tr(TE)$_n$Tr**, and their photophysical properties in solution and in thin film. We observed that compound **1** has a longer excited-state lifetime (10.1 ns) than

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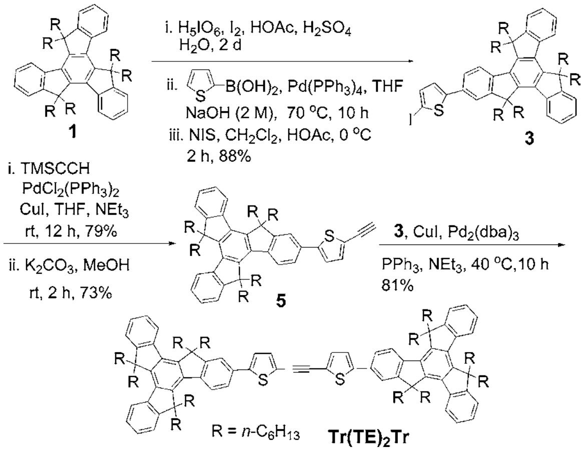
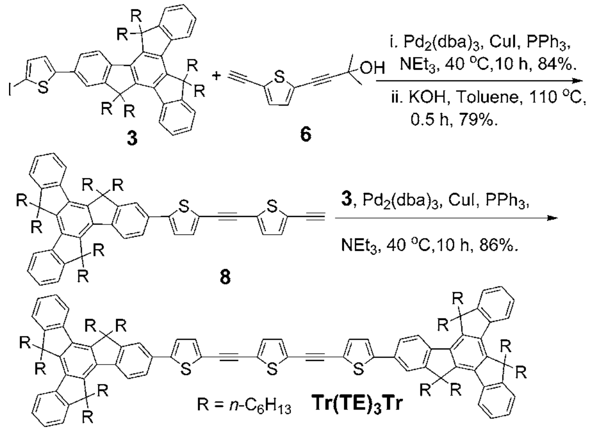
the lifetime of OTEs with a few hundred picoseconds. Our goal is to understand the relationship between the effective conjugation length and the photophysical properties as well as the excited-state lifetime in such molecular wires. The investigation indicates that the introduction of the truxene units as the end group not only effectively suppresses the formation of aggregates of these molecular wires in the ground state but also converts the single-exponential of the excited-state lifetime of OTEs to biexponential with a longer lifetime component, which makes it possible to employ such compounds for optoelectronic devices.

The synthesis comprises an iterative Pd-mediated Sonogashira coupling reaction.[6] Scheme 1 illustrates the synthetic approaches to **Tr(TE)$_2$Tr**. A reaction sequence of the iodination of **1** followed by a Suzuki coupling with 2-thiopheneboronic acid catalyzed by Pd(PPh$_3$)$_4$ and then treatment with *N*-iodosuccinimide (NIS) afforded **3** in 33% overall yield. A Sonogashira coupling of **3** with trimethylsilylacetylene followed by deprotection of the TMS group under basic conditions afforded **5** in 56% overall yield. The first molecular wire **Tr(TE)$_2$Tr** was obtained through the Sonagashira coupling between **3** and **5** in 81% yield. When trimethylsilylacetylene was used for the Sonogashira cross-coupling, catalyst PdCl$_2$(PPh$_3$)$_2$ was employed to give a reasonable yield. However, it afforded a very poor yield (<10%) when ethylnylenes with high molecular weight and/or large steric hindrance, for example, **5** (Schemes 1 and 3), **8** (Schemes 2 and 4), and **13** (Scheme 4), were used. A much higher yield was achieved through the replacement of PdCl$_2$(PPh$_3$)$_2$ by Pd$_2$(dba)$_3$. Therefore, Pd$_2$(dba)$_3$ was chosen to catalyze the Sonogashira cross-coupling of ethylnylene derivatives with high molecular weight and/or large steric hindrance, such as **5**, **8**, and **13**.

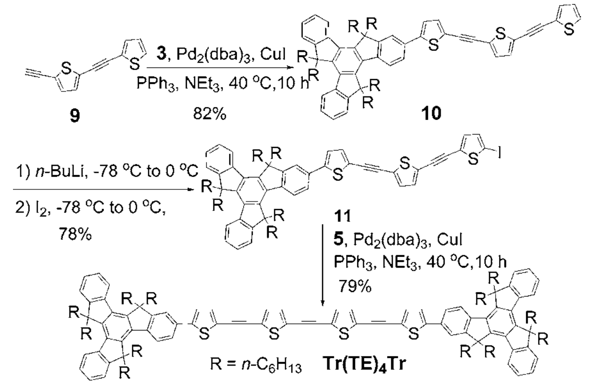
Scheme 1. Synthesis of **Tr(TE)$_2$Tr**



Scheme 2. Synthesis of **Tr(TE)$_3$Tr**



Scheme 3. Synthesis of **Tr(TE)$_4$Tr**



As shown in Scheme 2, a Sonogashira reaction between **3** and **6** followed by deprotection provided **8** in about 66% yield. Finally, **Tr(TE)$_3$Tr** was obtained through another Sonogashira reaction between **8** and **3** in 86% yield. Scheme

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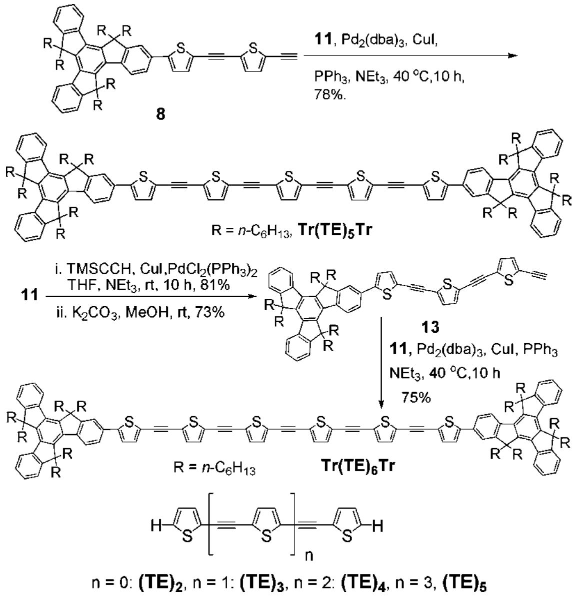
Scheme 4. Synthesis of **Tr(TE)$_5$Tr** and **Tr(TE)$_6$Tr**



3 outlines the synthesis of **Tr(TE)$_4$Tr**. A Sonogashira reaction of **3** with **9** afforded **10** in 82% yield. Following the typical iodination conditions with NIS, we did not obtain **11** and quantitatively recovered **10**, although NIS is a typical reagent for iodination of the thiophene ring. Prolongation of the reaction and/or heating did not result in improvement of the reaction. Other procedures were tested, and finally, iodination was achieved through the lithiation of **10** with n-BuLi at −78 °C followed by the addition of elementary iodine to afford **11** in 78% yield.[7] **Tr(TE)$_4$Tr** was obtained through the Sonogashira reaction between **11** and **5**.

As shown in Scheme 4, the Sonogashira coupling reaction between **8** and **11** afforded **Tr(TE)$_5$Tr** in 78% yield. For the synthesis of **Tr(TE)$_6$Tr**, the Sonogashira coupling between **11** and trimethylsilylacetylene followed by the deprotection of the TMS group achieved the terminal ethylnylene **13** in 59% yield. The Sonogashira coupling reaction of **13** with **11** afforded **Tr(TE)$_6$Tr** in 75% yield. Scheme 4 also show the structures of model compounds of **(TE)$_n$** ($n = 2-5$).[4a]

All compounds were readily soluble in common organic solvents, such as toluene, THF, and CH_2Cl_2. The structures and purity of all new compounds were fully characterized and verified by ^{1}H and ^{13}C NMR, elemental analysis, as well as MALDI-TOF MS (see the Supporting Information).

The photophysical properties of molecular wires **Tr(TE)$_n$Tr** ($n = 2-6$) were first investigated in dilute THF solution. Figure 1 shows their absorption and photoluminescent (PL) spectra in solution. Photophysical data from both solution and thin films are summarized in Table 1. All molecular wires exhibited an identical absorption at 308 nm with the same molar extinction coefficient ($\log \epsilon = 4.92$), which was assigned to the $\pi-\pi^*$ electron absorption band of truxene units.[8] It was also observed that their absorption λ_{max} peaked at 394 nm for **Tr(TE)$_2$Tr**, 409 nm for **Tr(TE)$_3$Tr**, 416 nm for **Tr(TE)$_4$Tr**, 422 nm for **Tr(TE)$_5$Tr**, and 424 nm for **Tr(TE)$_6$Tr**, respectively, which exhibited the continual red-shift in agreement with the increase of the effective conjugation length. Their molar extinction coefficient of absorption λ_{max} also gradually increased from **Tr(TE)$_2$Tr** to **Tr(TE)$_6$Tr**. In comparison with their corresponding OTEs, the obvious red-shift in absorption λ_{max} of these molecular wires was achieved due to the introduction of truxene units to improve the effective conjugation length of the whole molecular wire. For example, the absorption λ_{max} red-shifted about 77 nm for **Tr(TE)$_2$Tr**, 49 nm for **Tr(TE)$_3$Tr**, 39 nm for **Tr(TE)$_4$Tr**, 22 nm for **Tr(TE)$_5$Tr** relative to those of **(TE)$_2$** (317 nm), of **(TE)$_3$** (360 nm), of **(TE)$_4$** (377 nm), and of **(TE)$_5$** (400 nm), respectively.[4a,9] All PL spectra in solution showed a maximum peak with a shoulder on the red side. It was observed that the PL λ_{max} in dilute THF solution red-shifted from **Tr(TE)$_2$Tr** to **Tr(TE)$_6$Tr**. They also exhibited similar Stokes shifts (about 66 nm) due to their similar rigid backbone. Moreover, it was observed that both absorption and PL λ_{max} of **Tr(TE)$_6$Tr** red-shifted only 2 nm in comparison with those of **Tr(TE)$_5$Tr**, which indicated that the saturation of the effective conjugation length of this series of molecular wires was achieved around **Tr(TE)$_6$Tr**. Normally, the saturation of the effective conjugation length for OTEs is found at around the octomer range.[9] The fluorescence quantum yields (Φ_{PL}) of these molecular wires in dilute THF solution were measured to be 0.25 for **Tr(TE)$_2$Tr**, 0.22 for **Tr(TE)$_3$Tr**, 0.20 for **Tr(TE)$_4$Tr**, 0.20 for **Tr(TE)$_5$Tr**, and 0.18 for **Tr(TE)$_6$Tr**, respectively, using 9,10-diphenylanthracene as the standard.[10] Although decreased with an increase in the number of thiophene rings, their Φ_{PL}s were dramatically improved in comparison with those of OTEs due to the introduction of aromatic units with six-membered rings.[11]

The fluorescence decay parameters of these molecular wires in solution are collected in Table 1. Usually, the excited-state lifetime for OTEs was found to be single-expo-

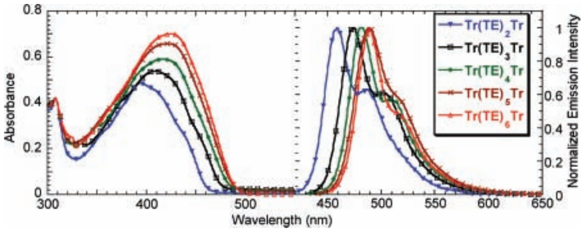


Figure 1. Absorption and PL spectra of **Tr(TE)$_n$Tr** ($n = 2-6$) in THF solution. PL spectra recorded under excitation at the absorption λ_{max} wavelength at room temperature.

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Table 1. Photophysical Properties of Molecular Wires in Solutions and in Thin Films

compd	λ_{max} (abs),^{a} nm (log ϵ)	λ_{max} (emis),^{b} nm	λ_{max} (abs),^{c} nm	λ_{max} (emis),^{c} nm	Φ_{PL},^{d} %	τ,^{e} ns (χ^2)
Tr(TE)$_2$Tr	308 (4.92), 394 (4.99)	460 (487)	309, 400	470, 491	25	0.42 (91.4%), 1.29 (8.6%), (1.075)
Tr(TE)$_3$Tr	308 (4.92), 409 (5.04)	474 (504)	309, 410	519	22	0.30 (97.8%), 1.70 (2.2%), (1.172)
Tr(TE)$_4$Tr	308 (4.92), 416 (5.08)	484 (512)	309, 415	525	20	0.32 (84.3%), 1.50 (15.7%), (1.162)
Tr(TE)$_5$Tr	308 (4.92), 422 (5.12)	488 (515)	309, 418	529	19	0.32 (88.5%), 1.85 (11.5%), (1.133)
Tr(TE)$_6$Tr	308 (4.92), 424 (5.15)	490 (516)	309, 424	515	18	0.31 (98.2%), 1.64 (1.8%), (0.990)

[a] In THF solution (5×10^{-6} M). [b] In THF solution (10^{-7} M); the shoulder peaks are shown in parentheses. [c] In thin films. [d] In THF solution (10^{-7} M) and 9,10-diphenylanthrancene as standard. [e] In THF solution (10^{-7} M); the fluorescence decay was monitored at the maximum emission peak. Both τ values denote the fluorescence lifetimes associated with the two exponentials obtained from the reconvolution fits. The percentage indicates the contribution of that component. All emission spectra were collected by the excitation at the absorption maximum of the corresponding compounds.

nential within a few hundred picoseconds.[9] However, in THF solutions (10^{-7} M), the decay of the emission maximum band for these molecular wires was found to be biexponential with two excited-state lifetimes yielding a χ^2 of less than 1.2. One excited-state lifetime ranged from 0.42 to 0.30 ns, which was in agreement with that in OTEs.[9] Another one exhibited a longer lifetime ranging from 1.29 to 1.85 ns. Given the lack of interchain interactions in dilute solutions, this emission was assigned to intrachain singlet excitons on the backbone. Therefore, the introduction of truxene units, which have long excited-state lifetimes (10.1 ns), might modify the excited-state lifetime of such molecular wires.

The absorption and PL spectra of these molecular wires **Tr(TE)$_n$Tr** ($n = 2-6$) in thin film were also measured. Figure 2 shows their absorption and PL spectra in thin film. The thin films were obtained by spin-coating toluene solution (ca. 10 mg/mL) onto quartz plates at 1000 rpm. All compounds exhibited excellent film-forming properties. The absorption spectra of every molecular wire (**Tr(TE)$_n$Tr**) in thin films were nearly identical with those in solution, which implied that the interchain interaction and/or intermolecular aggregation in the ground states might be suppressed in films possibly owing to truxene moieties with hexyl substituents. Therefore, these molecular wires exhibited different characteristics in the absorption spectra relative to other molecular wires, such as OTEs.[9] Their absorption spectra in films show an identical peak at about 309 nm owing to the $\pi-\pi^*$ electron absorption band of the truxene units. The absorption λ_{max} peaked at 400 nm for **Tr(TE)$_2$Tr**, 410 nm for **Tr(TE)$_3$Tr**, 415 nm for **Tr(TE)$_4$Tr**, 418 nm for **Tr(TE)$_5$Tr**, and 424 nm for **Tr(TE)$_6$Tr**, respectively. Such red-shifts were in agreement with an increase of the effective conjugation length. In comparison with those in dilute solutions, the PL spectra of these molecular wires in thin films became very broad and their maximum peaks were obviously red-shifted, for example, 10 nm for **Tr(TE)$_2$Tr**, 45 nm for **Tr(TE)$_3$Tr**, 41 nm for **Tr(TE)$_4$Tr**, 41 nm for **Tr(TE)$_5$Tr**, and 25 nm for **Tr(TE)$_6$Tr**, respectively, which indicated that the excimer for these molecular wires might be formed in the excited states. It was also observed that the PL λ_{max} gradually red-shifted from **Tr(TE)$_2$Tr** to **Tr(TE)$_5$Tr**. In comparison with that of **Tr(TE)$_5$Tr**, the PL λ_{max} of **Tr(TE)$_6$Tr** blue-shifted about 14 nm and also blue-shifted 4 nm relative to that of **Tr(TE)$_3$Tr**.

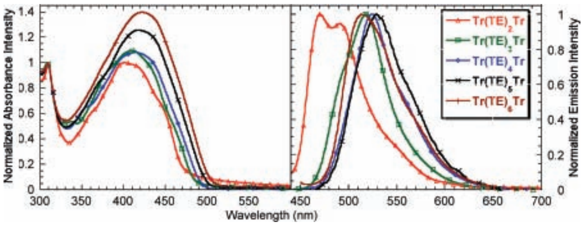

Figure 2. Absorption and PL spectra of **Tr(TE)$_n$Tr** ($n = 2-6$) in thin film. PL spectra recorded under excitation at the absorption λ_{max} wavelength at room temperature.

In conclusion, we have developed a new series of π-conjugated molecular wires based on thienylethynylene units, **Tr(TE)$_n$Tr** ($n = 2-6$), through the Sonogashira cross-coupling reaction in good yields. In comparison with OTEs, the obvious red-shift of λ_{max} of their absorption and PL spectra in dilute solution and in thin film is in agreement with an increase of the effective conjugation length. Introduction of truxene units not only suppresses the formation of aggregates at the ground state, but also modifies the excited-state lifetime from single exponential to biexponential. We are currently synthesizing a complete library of these molecular wires through various strategies and trying to pave the way for the investigation of these unique classes of precisely defined conjugated architectures.

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Supporting Information Available: Experimental procedures and ^{1}H and ^{13}C NMR, MS data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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