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Synthesis, theoretical and photophysical studies of mono-alkynylated tetrathienylethene via Sonogashira reaction: A useful tool for enhancement of their aggregation induced emission properties.

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ABSTRACT

The tetrathienylethene is firstly synthesized via a novel single step via Stille palladium(0) cross coupling reaction of tetrachloroethene with 2-(tributylstannyl)thiophene. The Sonogashira coupling reaction of bromotetrathienylethene with various alkynes are reported. Especially, their photophysical properties and aggregation induced emission effects of alkynylated tetrathienylethene are enhanced, tunable and characterized.

Introduction

Tetrathienylethene has gained significant attention as a new and easily functionalized building block in the realm of advanced materials, owing to its distinctive redox properties [1,2] and Aggregation - Induced Emission (AIE) characteristics. This organic compound, featuring four thiophene rings bonded to an ethene core, offers a remarkable platform for material innovation due to its highly adaptable chemical structure. The alpha positions on the thiophene rings are particularly noteworthy for their electron-rich nature, making them prime sites for functionalization[3–5]. This allows researchers to fine-tune the electronic, photophysical, and solubility properties of tetrathienylethene, tailoring it for a wide range of applications.

The AIE properties of tetrathienylethene are especially intriguing, as they enable the compound to exhibit enhanced emission in aggregated states, a feature that overcomes the limitations of traditional fluorophores that suffer from quenching when aggregated [6]. This makes tetrathienylethene [7] a valuable component in the design of efficient and stable luminescent materials, suitable for applications in bioimaging, sensors, and light-emitting devices. Additionally, its redox properties open up further possibilities for use in electronic and electrochemical devices, expanding its potential applications.

The combination of these properties makes tetrathienylethene an exceptional candidate for the development of novel organic semiconductors and photovoltaic materials. By semi-locked TTE structures with the combination of Triphenylamine 1, This building block exhibits an exceptional equilibrium between its molecular structure and hole-transporting capabilities, demonstrating potential for high-performance photovoltaic applications in the development of solution-processable organic semiconductors [8]. Liu in

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2018 had combined 2 AIEgens with a double bond 2 [3] resulting in long wavelengths and red fluorescent probes. With high aggregation enhanced emission (AEE) effect, 2 had the ability to specific staining cell membrane of Hela cells. The introduction of TTE to buckminsterfullerene C60[9] showed hole delocalization, which indicated 3 to be an efficient photoinduced charge-separation system in polar solvents. TTE functionalized by adding benzaldehyde 4 [10]experienced super red-shifted reversible mechanochromism and highly sensitive to hydrazine. Binuclear silver tetracarbene complexes 5[11] showed tunable fluorescence behavior in solvent mixtures and depending on the temperature (Figure 1).

In this article, a new convenient way to obtain functionalized TTE was first introduced, which then applies to alkylated TTE via Sonogashira reaction as well as the photophysical and theoretical characteristics of them were showed.

Experimental

Reagents and Materials.

Starting reagents were purchased commercially and used without further purification.

Measurement.

1H NMR spectra were recorded on a BRUKER 500 MHz Ascend spectrometer with tetramethylsilane (TMS) as the internal standard. UV−visible absorption spectra were obtained using Aligent Cary 5000. Steady-state fluorescence spectra and excitation spectra were measured using NanoLog Horiba.

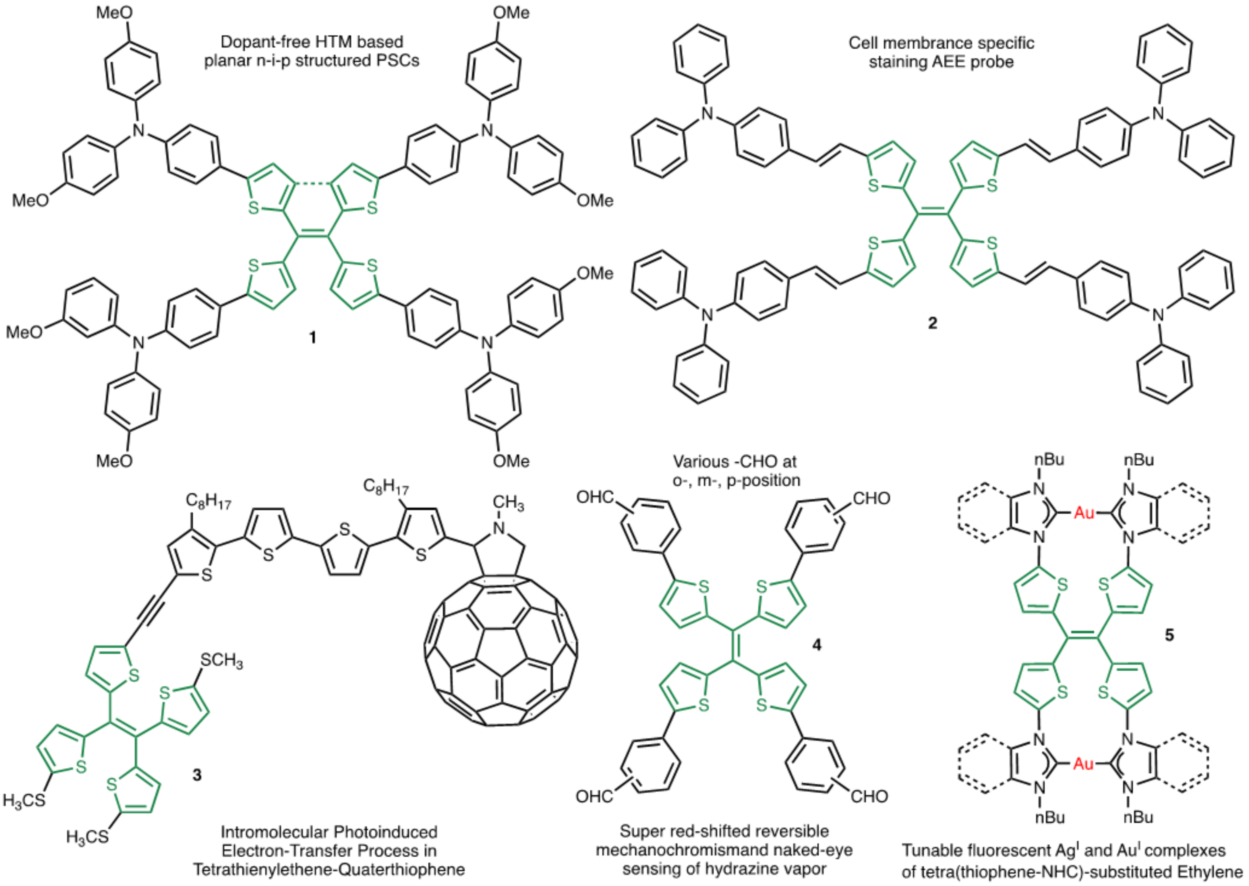
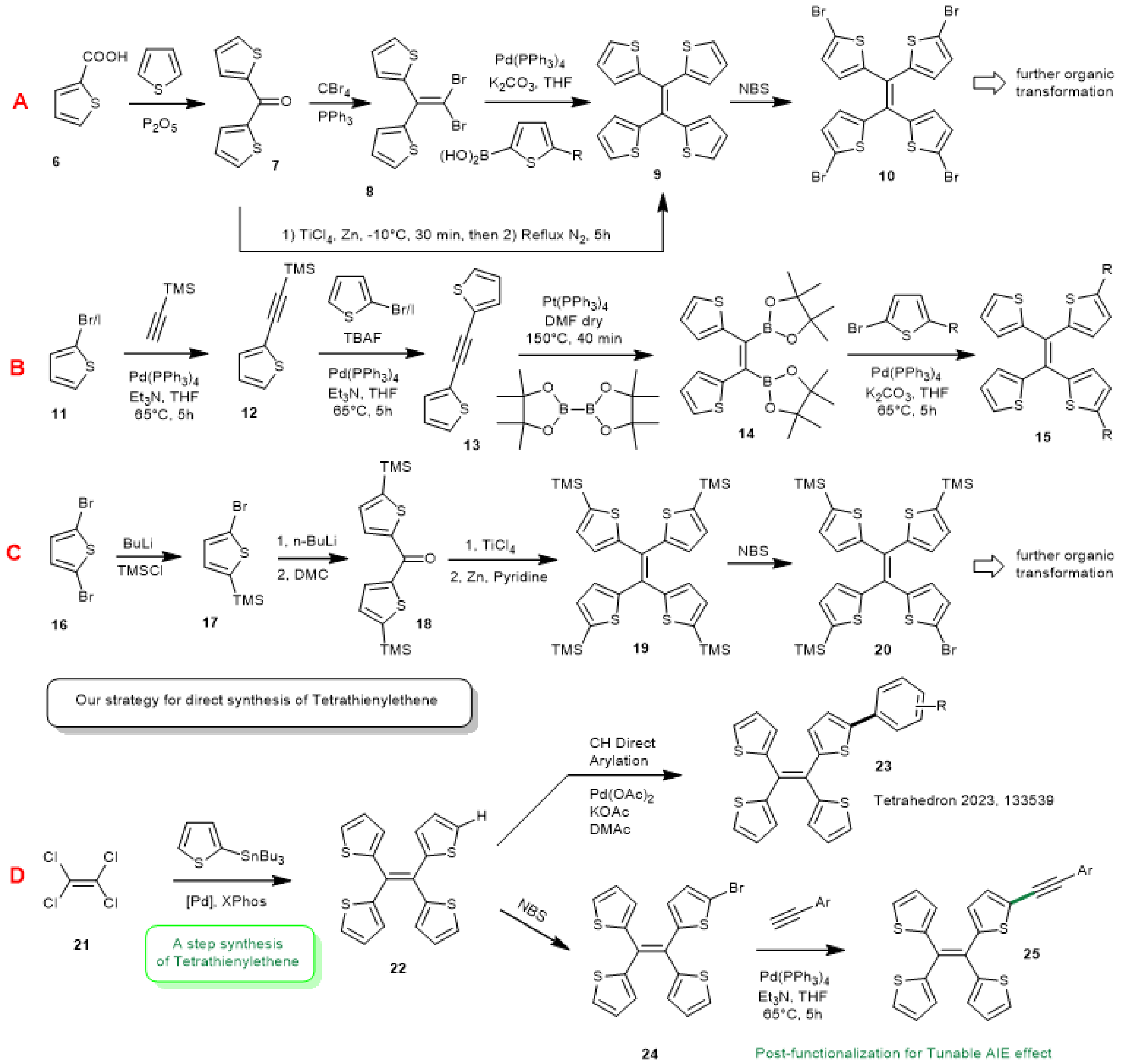


Fig. 1: Tetrathienylethene as important high π-conjugated system for various applications

General procedure for the synthesis of Tetrathienyl-ethene (22):

Tetrachlorethene 21 (600 mg, 3.6 mmol, 1 equiv.) and 2-(Tributylstannyl)thiophene (6.72 g, 18 mmol, 5 equiv.) were added to and oven-dried and argon flushed pressure tube equipped with magnetic stir bar. The mixture was purged with argon for 15 minutes. Afterward, Pd(OAc)2 (40.2 mg, 0.18 mmol, 5%) and Xphos (171.2 mg, 0.36 mmol, 10%) were added at once and the reaction mixture was purged with argon an additional two minutes and the tube was tightly sealed. The reaction mixture was stirred for 48 hours at 80°C. After cooling the reaction mixture to the room temperature, brine was added and the mixture was extracted 3 times with DCM. The organic layers were combined and dried over anhydrous Na_2SO_4. Organic solvents were removed under vacuum and the crude mixture was purified by a column chromatography on silica gel (hexane/ethyl acetate) affording compound 22 (770 mg, 60%) as a orange solid. $R_f = 0.4$ (SiO_2, hexane/ ethyl acetate, 20:1). The analytical and spectroscopic data are in agreement with those previously reported

General procedure for synthesis of mono alkylated tetrathienylethene (25a-e):



Scheme 1: (A-C)A few reported multi-step synthetic approaches for synthesis of functionalized tetrathienylethene. (D)Single step synthesis of Tetrathienylethene and post-functionalization.

Mono-brominated tetrathienylethene 24 (50 mg, 0.11 mmol, 1 equiv.), aryl acetylene (0.165 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (6.3 mg, 0.0055 mmol, 5%), CuI (2.5 mg, 0.0132 mmol, 12%), Et_3N (1 mL) and THF (4 mL) were added to and oven-dried and argon flushed pressure tube equipped with magnetic stir bar. The mixture was purged with argon and the tube was tightly sealed. The reaction mixture was stirred for 5 hours at 65°C. After cooling the reaction mixture to the room temperature, brine was added and the mixture was extracted 3 times with DCM. The organic layers were combined and dried over anhydrous Na$_2$SO$_4$. Organic solvents were removed under vacuum and the crude mixture was purified by a column chromatography on silica gel (hexane/ethyl acetate) affording compound 25a-e.

Results and discussion

Despite Tetrathienylethene's (TTE) unique properties its synthetic scheme was still included many steps with moderate yield and harsh conditions. Traditionally, the synthesis scheme of TTE requires 4-5 steps to get to the final functionalized TTE. Its traditional synthesis originally required a two-step process introduced by Miyashi in 1992 (Scheme 1A)[1]. This method involved starting from 2-thiophenecarboxylic acid, where a C-C bond cleavage reaction yielded bis(2-thienyl)ketone. Subsequently, the McMurry coupling method, utilizing TiCl$_4$/Zn[12], was employed to achieve the final formation of TTE. This approach gained widespread [13,14] use until 2013, when Licandro [2] introduced an alternative synthetic route, simplifying the process (Scheme 1B). Despite advancements, 1,2-dithienylalkyne remains a commercially viable starting material, undergoing two sequential reactions namely platinum-catalyzed syn-diboration and Suzuki to synthesize TTE. Another synthesis strategy to obtain bis(2-thienyl)ketone was introduced by Wang [13] in 2012, which involved of organolithium followed by McMurry coupling reaction. (Scheme 1C). Herein, we have successfully synthesized TTE in single step by Stille cross coupling reaction of 2-(tributylstannyl)thiophene into tetrachlorethene and this was applied to synthesis post-functionalized TTE (Scheme 1D). [15]

The Stille cross coupling reaction of 2-(tributylstannyl)thiophene into tetrachlorethene was examine for the optimized conditions. Various conditions were taken (Table 1A).

By changing the type of Palladium source, ligands and types of reactions, an optimal condition was found. Suzuki reaction was also examined but no reaction was found. For the optimal concentration for reaction, no solvents was used as both of tetrachloroethene and 2-(tributylstannyl)thiophene are liquid. Under neat conditions with palladium acetate and Xphos and potassium phosphate was TTE obtained with 60% yield. Xphos proved to be the most suitable ligand for this reaction due to its performance with palladium acetate and Pd$_2$(dba)$_3$. Although there were some changes in yield when increasing the temperature, 80^{o}C was the optimal temperature for 2 days for this to react.

In order to further characterize, TTE was brominated for further functionalization. Condition screening was showed in figure 1. Alpha position of thienyl ring is electron rich, therefore, it is easily to bromination and the equivalent of brom reagent have to be precise. By remaining the temperature at 0^{o}C, and for long hours, brominated TTE was obtained with 98% yield.

To functionalize mono bromine TTE, Sonogashira reaction was used. At first, phenylacetylene was examined for screening the condition. By using Pd(PPh$_3$)$_4$, CuI as catalyst in Et$_3$N and THF solvent at 65^{o}C for 5 hours, the mono trimethylsilylacetyl TTE was obtained with good yield. Applying this condition to other derivatives gave other 4 mono coupling with moderate to good yield (60 to 70%). However, this optimal condition was only applied to electro-directing groups. Under the condition, electro-withdrawing group of acetylene gave no reactions.

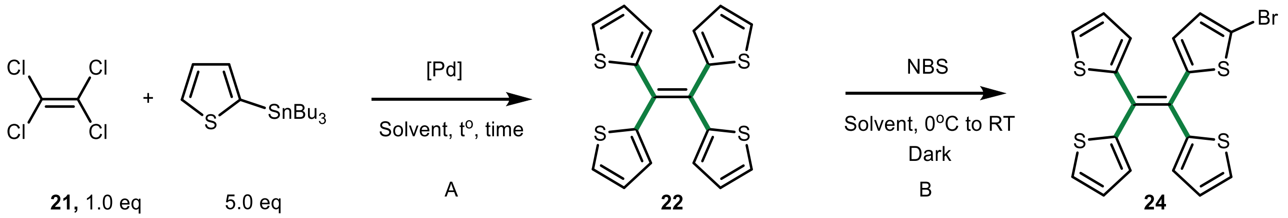


Table 1: (A)Screening conditions of synthesis of tetrathienylethene 22
(B) Screening synthetic conditions of 2-bromothien-5-yl1,1,2-trithienylethene 24

Condition A: Tetrafold coupling reaction						**Condition B**: Monobromination reaction				
En	[Pd] (eq)	Ligand (eq)	Solv.	Con.	Yield (%)	22 (eq)	NBS (eq)	Solv.	Con.	Yield (%)
1	$Pd(PPh_3)_4$ 0.05	-	Toluene	80 °C, 48h	low	1.0	1.1	DMF	0 °C, 1h	11
2	$Pd(PPh_3)_4$ 0.05	-	Toluene	120 °C, 48h	20	1.0	1.1	DMF	0 °C, 3h	30
3	$Pd_2(dba)_3$ 0.05	XPhos 0.2	-	80 °C, 48h	30	1.0	1.1	DMF	0 °C, 12h	60
4	$Pd(OAc)_2$ 0.05	PCy_3 0.1	-	80 °C, 48h	n.r.	1.0	1.1	DMF	0 °C, 24h	98
5	$Pd(OAc)_2$ 0.05	XPhos 0.1	-	80 °C, 48h	60	1.0	1.1	DMF	M.W, 30°C, 1h[b]	n.r.
6	$Pd(OAc)_2$ 0.05	XPhos 0.1	-	120 °C, 48h	50	1.0	1.1	DMF	M.W, 30 °C, 1h	low
7	$Pd(OAc)_2$ 0.04	PPh_3 0.08	Dioxane/ H_2O 4:1	120 °C, 48h	n.r.[a]	1.0	1.1	DMF	M.W, 30 °C, 12h	20

[a] Thienyl Source : 2-Thienylboronic acid (5.0 eq.)

All the reactions were proceeded in the dark

[b] The reaction was proceed in the light

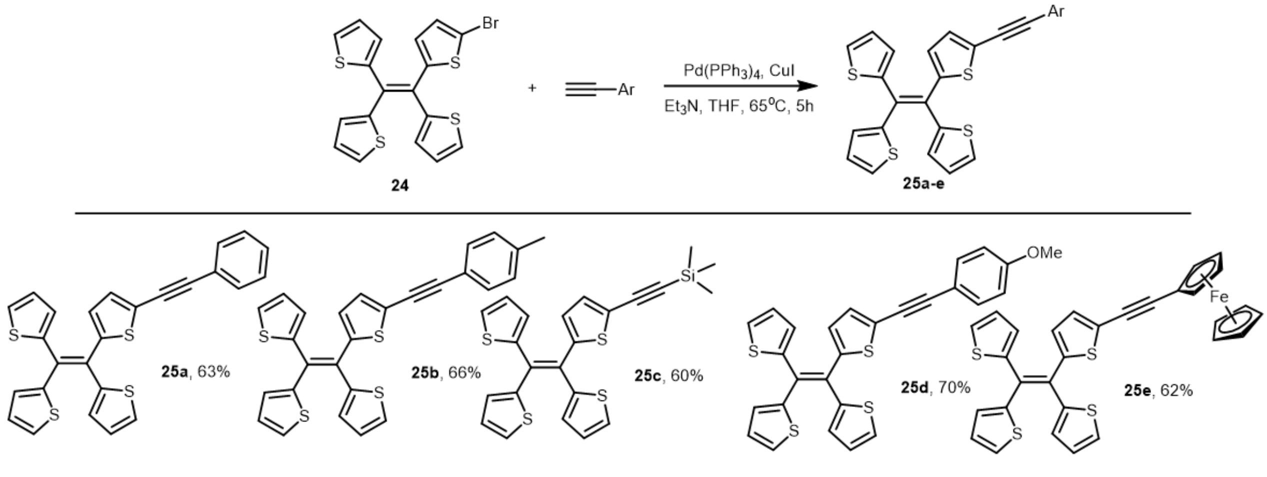


Figure 2: Screening monoalkynylated tetrathienylethene derivatives

Conclusion

In conclusion, a new and convenient pathway to synthesis tetrathienylethene (TTE) was introduced. Only via 1 step of cross coupling reaction from tetrachloroethene, a commercially available chemicals, TTE was synthesized under mild conditions for relatively good yield. This is the first time an AIE luminophore synthesized single step, which pave a new and easier way to introduce AIE scaffold into any desired molecules. Furthermore, a series of post-functionalized TTE was obtained by bromination and then Sonogashira reaction for investigating AIE potentials. Successfully single step synthesis of TTE and alkylnylated post-funtionalization show a great potential for introducing AIE linkers to apply in various field such as OLED, sensors and organic photovoltaics.

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