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Divergent and Stereoselective Synthesis of Tetraarylethylenes from Vinylboronates

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Dedication to the 20th Anniversary of Aggregation-Induced Emission (AIE)

ABSTRACT: We here report the synthesis of a new tetraborylethylene (TBE) and its application in the preparation of [4+0]-tetraarylethenes (TAEs) that have widespread applications in material science and supramolecular chemistry due to their aggregation-induced emission (AIE) nature. The divergent and stereoselective synthesis of [3+1]-, [2+2]-, [2+1+1]-TAEs via multicouplings of vinylboronates with aryl bromides were also demonstrated. These couplings feature broad substrate scope and excellent functional group compatibility due to mild reaction conditions, providing facile access to various tetraarylethenes. This strategy represents an important complement to the conventional methods for the synthesis of TAEs, and would be a valuable tool for synthesizing TAE-based molecules used in functional material, biological imaging and chemical sensing.

Introduction

Tetraarylethylenes (TAEs) exhibit intriguing chemical and physical properties due to their geometric and electronic features, and have extensive applications in materials science,^[1] synthetic and biological chemistry.^[2] and supramolecular frameworks.^[3] For instance, TAE-a and TAE-b are broadly utilized in platinum-coordination driven self-assembly^[4] and the construction of metal-organic framework (MOF).^[5] and **TAE-c** is a versatile building block in the synthesis of covalent organic frameworks (COF) via imine formation (Figure 1a).^[6] In addition, since the concept of aggregation-induced emission (AIE) was originally proposed by Tang in 2001,^[7] the TAEs and their derivatives as AIE-active molecules have shown numerous applications in biological probes and imaging, chemical sensing, optoelectronic and stimuli-response materials.^[8] For example, Tang and Sun demonstrated that TAE-d can be used as a biosensor for selective D-glucose detection from a saccharide mixture in aqueous media.^[8b] Liu and coworkers have developed an elegant bioprobe with TAE-e as an imaging structural unit and photosensitizer for photodynamic therapy of cancer cells (Figure 1a).^[8g]

The tetraarylethylenes used in chemistry and materials science in the last two decades can be divided into 5 groups based on the categories of aryl groups, i.e., [4+0]-, [3+1]-, [2+2]-,

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[2+1+1]-, and [1+1+1+1]-TAEs (Figure 1b). Among them, although [4+0]- and [3+1]-TAEs have no stereoisomers, [2+2]- and [2+1+1]-TAEs engross 3 stereoisomers, respectively. In addition, [1+1+1+1]-TAEs are structurally diverse with up to six stereoisomers. The diversity of TAEs undoubtedly provides a powerful platform for the development of functional molecules and materials, but their stereoselective synthesis challenges synthetic chemists. For example, the synthesis of pure *E*-[2+2]- and *Z*-[2+2]-TAEs so far still rely on HPLC separation or the





Figure 1. The applications and classification of tetraarylethylene.

introduction of polar or unique functional groups,^[9] such as triazole^[9a, 9b] and oxetane,^[9d] to enlarge the difference between Z and E isomers in the shape and polarity. The divergent and stereoselective synthesis of TAEs is still challenging and remains to be deciphered, but it is highly desirable as it is the precondition for the elucidation their of structure-property-function relationships. Moreover. stereoisomers probably present marked difference in molecular properties and functions due to their different configurations. [8d,

Conventionally, tetraarylethylenes are usually synthesized from diarylketones via the McMurry reaction in the presence of titanium and zinc (eq 1, Figure 2a).^[10] However, the McMurry reaction suffers from restricted substrate scope and poor functional-group compatibility due to the use of strong Lewis

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Figure 2. Synthesis of tetraarylethylene.

acid $(TiCl_4).^{[10]}$ Furthermore, stereoselectivity control is still an unsolved issue in the McMurry reaction. Specifically, as for selfcoupling, the use of unsymmetrical diarylketone would generate an E/Z mixture of TAEs, which is mostly inseparable by column chromatography.^[10d] With regard to cross-coupling, poor stereoselectivity is also obtained when either symmetrical or asymmetrical diarylketones are utilized. Additionally, the selfcoupling is a quite competitive reaction in cross-coupling, resulting in low-yield formation of the desired TAEs and separation issues.^[10d] To avoid these problems, other strategies have been developed for the preparation of unsymmetrical TAEs. For instance, Rathore and co-workers disclosed an elegant method for the coupling of benzophenone with diarylmethane in the presence of organolithium and acid (eq 2, Figure 2a), which is suitable for the synthesis of [4+0]-, [3+1]-, and gem-[2+2]-TAEs.^[11] However, the stereoselectivity control is a formidable challenging for this protocol in the synthesis of E/Z-[2+2] and [2+1+1] TAEs. Furthermore, a range of functional groups such as aldehyde, ester, and nitrile are incompatible due to the use of organolithium compounds and acid. Pd-catalyzd Suzuki-Miyaura coupling of 1,1-dibromoalkene with arylboronic acid is also an attractive alternative for the TAE synthesis (eq 3, Figure 2a).^[12] Although this method is an efficient strategy for preparing geminal-substituted TAEs, it is inapplicable to the synthesis of other kinds of TAEs. Moreover, Pd-catalyzed alkyne-diarylation with an organometallic reagent allowed facile access to the unsymmetrical TAEs (eq 4, Figure 2a).^[13] Notably, the ability to simultaneously introduce two aryl groups makes this protocol appealing, but the regioselectivity control is still problematic (e.g. when $Ar^2 \neq Ar^3$). In common, these approaches suffer from poor stereoselectivity and limited substrate scope, and require either multi-step synthesis of starting materials or the use of organometallic reagents. Consequently, the development of a general, especially stereospecific method to streamline the preparation of TAEs is in great demand.

The Suzuki-Miyaura cross coupling is among the most extensively used method for forging C-C bonds in chemical synthesis, pharmaceutical industry, and materials science due to its mild reaction conditions and well-precedented functional group compatibility.^[14] Not surprisingly, the synthesis of

tetrasubstituted olefins based on Suzuki-Miyaura cross coupling has garnered considerable attention, and significant progress has been described in the formation of di- and tri-arylated alkenes.^[15] However, the preparation of tetraarylethylenes using Suzuki-Miyaura reaction has been little explored. The existing protocol focuses on the coupling of *gem*-dibromides with arylboronic acids.^[12] Taking into account the rapid development of vinylboronate synthesis,^[16] and the fact that there are more aryl electrophiles (i.e. aryl halides) listed as commercially available than aryl nucleophiles (i.e. arylboronic acids), we envision that the coupling of vinylboronates with aryl halides would be a promising strategy for the synthesis of TAEs.

Vinylboronates have found widespread applications in the introduction of C–C double bonds into various functional molecules via Suzuki-Miyaura cross coupling.^[17] The vinylboronates employed so far are mainly limited to monoborylalkenes that undergo single coupling with aryl halide. The examples of double couplings for diborylalkenes are rare and triple and quadruple couplings, to the best of our knowledge, are yet to be reported, although diborylalkenes and triborylalkenes can be readily synthesized by Pt-catalyzed diboration reaction.^[18]

Herein, we describe the preparation of tetraarylethylenes from di-, tri-, and tetra-borylalkenes via the corresponding double, triple, and quadruple Suzuki-Miyaura couplings with good efficiency and stereoselectivity (Figure 2b), which provides a facile and efficient protocol for synthesizing various functional TAE molecules.



Figure 3. Synthesis of tetraborylethylene.

Results and Discussion

In principle, tetraborylethylene (TBE) coupled with aryl halides would be the most straightforward method for the synthesis of tetraarylethylenes. However, this process has never been achieved as there is no protocol available for the synthesis of TBE that is suitable to the Suzuki-Miyaura coupling. The lone example to make TBE was reported by Siebert in 1996^[19]. Unfortunately, the TBE made by Siebert is inapplicable to Suzuki-Miyaura coupling due to its base sensitivity. Since pinacol boronates are significantly more stable than catechol boronates,^[20] we envision that tetraborylethylene 1 derived from pinacol would be applicable to TAE synthesis using the Suzuki-Miyaura reaction. To this end, we started our investigation by preparing TBE 1. We found that the TBE 1 could be readily prepared from commercially available and inexpensive trichloroethylene in high efficiency. The lithiation of trichloroethylene by n-BuLi generated dilithium acetylide intermediate. which was then trapped bv [/]PrOBpin (isopropoxyboronic acid pinacol ester) to give diborylacetylene A.

Table 1. Synthesis of [4+0]-tetraarylethylenes.[a]

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[a] Reaction conditions: **TBE** (0.2 mmol), aryl bromide (0.96 mmol), Pd(dppf)Cl₂ (0.01 mmol), Cs₂CO₃ (1.2 mmol), H₂O (40 µL), dioxane (3 mL) at 70 °C for 48 h. Isolated yields. [b] KOH was used as base and DME as solvent.

The subsequently Pt-catalyzed diboration afforded the desired TBE 1 (Figure 3). No chromatographic purification is required, and the reaction can be performed on a multigram scale, allowing easy access to TBE 1. It is worth mentioning that TBE 1 is air-stable and can be stored under an ambient atmosphere for months without decomposition.

With the tetraborylethylene 1 in hand, we next investigated the Suzuki-Miyaura coupling of TBE 1 with aryl bromides for the preparation of symmetric [4+0]-tetraarylethenes using 4bromotoluene as the model substrate. After exploring a series of reaction parameters, the use of TBE, aryl bromide (4.8 equiv), $Pd(dppf)Cl_2$ (5 mol%), and Cs_2CO_3 (6.0 equiv) in dioxane with H₂O at 70 °C for 48 h afforded the desired TAE 5aa in good yield. Noticeably, all the TAE products can be purified by routine silica gel chromatography (see more details on purification methods in SI). We then examined the generality of the aromatic bromide substrate for this quadruple Suzuki-Miyaura coupling, and the results are summarized in Table 1. As shown, a wide range of aryl bromides with various substituents at different positions all successfully participated in this reaction to afford the desired tetraarylethylenes in moderate to excellent yields. A series of functional groups, such as methoxyl (5ac), methylthio (5ad), protected alcohol (5ag), nitrile (5aj), trifluoromethyl (5al), and chloride (5am), were all tolerated under the mild reaction conditions. Of particular note, the functional groups incompatible with the McMurry reaction conditions, including amide (5ae), formyl (5ah), acetyl (5ai), and ester (5ak), remain intact to produce the corresponding TAEs in moderate

to excellent yields. Notably, the products 5ah-k can be used as (precursors) building blocks for the synthesis of MOF, COF, and/or self-assembled metallacages. Furthermore, the vinyl group was compatible to provide TAE 5an amenable for further downstream diversification via alkene functionalization. It is worth noting that TAE **5ao-ap** with a pyridyl that exhibit wide applications in metal-coordination driven self-assembly, previously required multiple-step synthesis and now can be synthesized by a single-step procedure with moderate efficiency. In addition, multi-substituted aryl bromides also reacted smoothly with TBE 1 to deliver TAE 5ar-at, which are challenging for the existing methods. Likewise, naphthalenes (5au-aw) were tolerated for these quadruple couplings. AlEgens bearing heterocycles have drawn attention due to their unique distinctive electronic structures, and the lack of efficient approaches for their synthesis encourage our attempt to prepare them using this four-fold coupling reaction. A range of heteroaromatic rings, such as indole (5ax), benzofuran (5ay), benzothiophene (5az), benzothiadiazole (5ba), and carbozole (5bb) were competent substrates, providing the desired products in moderate to good yields. These results highlight the excellent substrate diversity and high efficiency of this coupling reaction for the synthesis of symmetrical [4+0]-tetraarylethylenes, especially those bearing reactive functional groups.

The conventional methods for synthesizing [3+1]-TAE such as McMurry reaction typically result in low efficiency due to the inevitably competing homo-coupling reactions.^[21]





[a] Reaction conditions: 2 (0.2 mmol), aryl bromides (0.72 mmol), Pd(dppf)Cl₂ (0.01 mmol), Cs₂CO₃ (0.9 mmol), H₂O (40 µL), dioxane (3 mL) at 70 °C for 36 h. Isolated yields.

Table 3. Synthesis of [2+2]- and [2+1+1]-tetraarylethylenes.[a]



[a] Reaction conditions: 2 (0.5 mmol), aryl iodide (0.5 mmol), Pd(PPh₃)₄ (0.05 mmol), K₃PO₄ (1.5 mmol), H₂O (1 mL), THF (4 mL) at 70 °C for 24 h (the first step); *E*-3 (0.2 mmol), aryl bromides (0.48 mmol), Pd(dppf)Cl₂ (0.01 mmol), Cs₂CO₃ (0.6 mmol), H₂O (40 μL), dioxane (3 mL) at 70 °C for 24 h (the second step). Yields given were isolated yields for the second step.

Table 4. Synthesis of [2+2]- and [2+1+1]-tetraarylethylenes.[a]

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[a] Reaction conditions: Z-3 (0.2 mmol), aryl bromide (0.48 mmol), Pd(dppf)Cl₂ (0.01 mmol), Cs₂CO₃ (0.6 mmol), H₂O (40 μL), dioxane (3 mL) at 70 °C for 24 h. Isolated yields. Py = 4-pyridyl.

Table 5. Synthesis of [2+2]- and [2+1+1]-tetraarylethylenes.[a]



[a] Reaction conditions: 4 (0.2 mmol), aryl bromide (0.48 mmol), Pd(dppf)Cl₂ (0.01 mmol), Cs₂CO₃ (0.6 mmol), H₂O (40 µL), dioxane (3 mL) at 70 °C for 24 h. Isolated yields. Py = 4-pyridyl.

Encouraged by the success of synthesizing [4+0]-TAEs, we turned our attention to the synthesis of [3+1]-TAEs using Suzuki-Miyaura reaction. We conjectured that the Pd-catalyzed quadruple couplings of TBE **1** involve a triborylalkene intermediate generated from TBE **1** via single coupling with ayrl bromide. Accordingly, triborylalkenes generated from alkynyl boronates via Pt-catalyzed diboration were used under the standard reaction conditions for the formation of [4+0]-TAEs, and the tri-coupled products were afforded in moderate to excellent yields. As shown in Table 2, a variety of aryl bromides can be employed for this triple

coupling reaction, regardless of the position as well as electronic nature of the substituents. Specifically, substrates bearing functional groups, such as acetyl, ester, chloride, amide, trifluoromethyl, formyl, pyridyl, and sulfonyl were welltolerated and provided the desired tri-coupled products in good to excellent yields. With respect to the triborylalkene, para- and meta-monosubstituted ones were found to be suitable substrates in this transformation (**5bl-br**). Moreover, the reaction was amenable to the triborylalkenes with electron-withdrawing and electron-donating groups, including methoxyl, fluoride, chloride, and protected alcohol.

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Figure 4. (a) **5ax** (20 μM) in THF–water mixtures with different volume fractions of water, photographs taken upon excitation at 365 nm using an UV lamp at 298k. (b) Normalized absorption spectra (dotted lines) and fluorescence emission spectra (solid lines) in DCM (1 × 10 ⁻⁵ M). (c) Synthesis of TPE-core crown ether.

The greatest challenge in the synthesis of tetraarylethylenes is the control of stereoselectivity that is of importance for the systematic dissection of the relationships between structure and function. Although stereoselectivity control is not an issue for the preparation of [4+0]- and [3+1]-TAEs, it is a great challenge for synthesizing [2+2]-, [2+1+1]-, and [1+1+1+1]-TAEs. Recently, Ozerov disclosed the lone example of a Pd-catalyzed Suzuki-Miyaura coupling of triborylalkene with 4-iodoanisole when they studied the synthesis of triborylalkenes from terminal alkynes that showed excellent stereoselectivity to give the *trans*-diborylalkene product.^[22] Inspired by this precedent, we hypothesized that the stereoselectivity issue for the synthesis of [2+2]- and [2+1+1]-TAEs may be addressed by a stereoselective Suzuki-Miyaura coupling. Hence, we reacted the triborylalkenes and aryl iodides under the reaction conditions reported by Ozerov. E-diborylalkene 3 were obtained in excellent stereoselectivity and moderate to good yields (Table 3), and E-3 was subjected to the quadruple coupling conditions. Pleasantly, the mild reaction conditions delivered the corresponding bicoupled products in excellent stereoselectivity and in yields ranging from 55% to 80% (Table 3). The stereochemistry was unambiguously assigned by X-ray crystallographic analysis of 5bv. The functional groups are well tolerated including chloride, ester, ketone, and sulfonyl. Furthermore, the efficiency of the reaction was not affected when polycyclic and heterocyclic substrates such as naphthalene, pyridine, and carbazole were employed. Moreover, [2+1+1]-TAEs can also be obtained via this stereospecific tandem Suzuki-Miyaura couplings. For instance, TAEs 5ca-cd with two pyridyls were isolated in good yields.

We next tested the viability of such Suzuki–Miyaura coupling for the synthesis of Z-[2+2]-TEAs from Z-diborylalkenes **3**, which could be readily prepared via Pt-catalyzed diboration of alkynes. Various aryl bromide with diverse substituents proved to be suitable coupling partners, affording Z-[2+2]-TEAs with excellent stereoselectivity (Table 4). Heteroarenes such as pyridine (**5ci**) and carbazole (**5cj**) were all viable in this coupling, and the reaction was also viable for functionalized diborylalkenes, furnishing TAEs **5ck-cm**. Furthermore, tetraarylethylenes other than [2+2]-TEAs, such as [2+1+1]-TAEs (**5cn-cp**), were also obtained from *Z*-diborylalkenes **3**.

Finally, we aimed to synthesize gem-[2+2]-TEAs from gemdiborylalkenes 4. As depicted in Table 5, the coupling was found to be tolerant to functional groups, including chloride, formyl, ester, sulfonyl, and pyridyl, and provides a platform for the construction of structurally complex molecules. The [2+1+1]-TAEs **5da-db** were also obtained from unsymmetrical gemdiborylalkenes 4 in good yields and excellent stereoselectivity.

With numerous tetraarylethylenes in hand, the photophysical properties were investigated by using representative AIEgens. As shown in Figure 4a, AIE was observed by dissolving 5ax in THF and water mixture with different fractions of water. Non- or weak emission was observed when the fraction of water was less than 60%, but the fluorescence intensity increased greatly when the water content reached 90 vol %. The absorption and emission spectra of representative tetraarylethylenes were also measured. As seen in Figure 4b, 5ad and 5al displayed broad absorption bands at 351 and 308 nm, respectively. In addition, AIEgens 5bx and 5cj showed similar absorption bands centered at 325 nm, and two absorption bands centered at 270 and 348 nm were observed for 5cl. With regard to the emission spectra, these luminogens showed emission maxima at approximately 480-530 nm. These multi-coupled products exhibit large Stokes shifts, making them potentially promising for biological imaging and detections.^[1f] It is also worth noting that electron-donating groups could induce red-shifts in the emission spectra (5ad vs 5al), which enable this multi-coupling protocol to prepare nearinfrared TAEs with large Stokes shift.





Figure 5. (a) Synthesis of **7a-c** via self-assembly of **5ch**, **5ck**, and **5cl** with **6**. (b-e) Partial ¹H NMR spectra (400 M, CDCl₃, 293 K) of ligand **5ch**, and **7a-c**. (f-i) Partial ³¹P{1H} NMR spectra (162 M, CDCl₃, 293 K) of diplatinum acceptor **6**, and **7a-c**. (j-k) Absorption and fluorescence emission spectra of **7a-c** in DCM (λex = 365 nm, 10 μM).

To demonstrate the robustness and synthetic utility of this protocol, TPE-core crown ether 5dc was synthesized in a single step and convergent procedure with 61% yield via the quadruple Suzuki-Miyaura couplings of TBE (Figure 4c). Of note, the TPEcore crown ether could form cross-linked supramolecular polymeric network with ammonium salt via host-guest interaction,[4f] and might find applications in construction of functional materials. In light of the facile preparation of heteroaromatic TAEs via the couplings of vinylboronates and their extensive applications in coordination-driven self-assembly, the usefulness of this strategy was further demonstrated by the construction of organoplatinum(II) metallacycles (Figure 5). The rhomboid platinum (II) metallacycles 7a-c were prepared from 60° TAE-based dipyridyl ligand (5ch, 5ck, 5cl) and 120° diplatinum acceptor 6. The formation of TAE-decorated metallacycles 7a-c was confirmed by multinuclear NMR (1H and ³¹P) analysis as well as ESI-TOF-MS. In the ¹H NMR spectrum (Figure 5c-e), the downfield shifts of the H_{a-c} protons of the pyridine were observed, indicating the formation of the Pt-pyridyl coordination bond. As illustrated in Figure 5g-i, the ³¹P{¹H} NMR spectra of **7a-c** and sharp singlets at δ = 15.48, 15.62, 15.53 ppm with concomitant ¹⁹⁵Pt satellites, respectively, suggesting a single phosphorus environment. These peaks are shifted upfield in comparison with the signal of the di-Pt(II) acceptors 6 (Figure 5f) by about 6.28, 6.14 and 6.23 ppm, respectively. Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) also provides evidences for the stoichiometry of metallacycles 7a-c by possessing isotopically well-resolved peaks that are in good agreement with the calculated theoretical distributions (see SI for details). Figure 5jk depict the UV-vis absorption and emission profiles of 7a-c. These three rhomboids displayed a broad absorption band centered at 365 nm. The emission maximum of the metallacycles 7a-c are at 540 nm, 540 nm, 590 nm, respectively (Figure 5k). Interestingly, the emission spectra of 7c shows a red shift to the near-infrared (NIR) region (650-900 nm) probably due to its donor- π -acceptor structure. Based on these results, we envision that the metallacycles with NIR emission

may be prepared via tuning the donor and acceptor units, and they might be useful for living animal imaging.^[4c,23]

Conclusion

In conclusion, we have prepared a tetraborylethylene (TBE) and demonstrated its application in the synthesis of [4+0]tetraarylethylenes via quadruple Suzuki-Miyaura couplings. The stereoselective synthesis of [3+1]-, [2+2]-, and [2+1+1]tetraarylethylenes from the corresponding vinylboronates and halides were also established, which provides a arvl synthetically useful tool for the preparation of novel TAE-based functional molecules. This protocol enabled the efficient preparation of pure E- and Z-[2+2]-TAEs, which represents an important complement to the existing methods that require multistep synthesis or have separation issues. The synthetic utilities were illustrated by the construction of TPE-core crown ether and the application of heteroaromatic TAEs in coordination-driven self-assembly. Further applications based on this new tetraborylethylene and the synthesis of new functional molecules and materials via this unprecedented multi-coupling are now under investigation in our lab.

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Conflict of interest

The authors declare no competing financial interests.

Keywords: aggregation-induced emission • tetraarylethylenes • fluorophores • boron • vinylboronates

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RESEARCH ARTICLE



We here report the synthesis of a new tetraborylethylene (TBE) and its application in the preparation of [4+0]-tetraarylethenes (TAEs). The divergent and stereoselective synthesis of [3+1]-, [2+2]-, [2+1+1]-TAEs via multi-couplings of vinylboronates with aryl bromides were also demonstrated. This strategy represents an important complement to the conventional methods for the synthesis of TAEs, and would be a valuable tool for synthesizing TAE-based molecules used in functional material, biological imaging and chemical sensing.

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Divergent and Stereoselective Synthesis of Tetraarylethylenes from Vinylboronates