

Modular Synthesis of Diarylalkynes and Their Efficient Conversion into Luminescent Tetraarylbutadienes

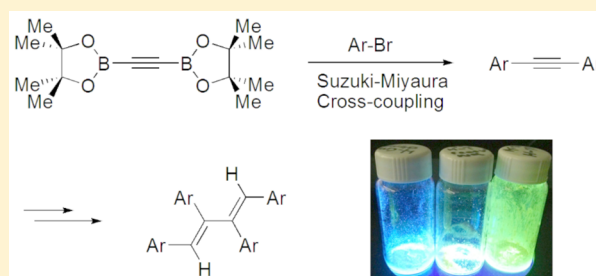
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S Supporting Information

ABSTRACT: A series of electronically distinct symmetrical diarylalkynes were prepared via a general Suzuki–Miyaura cross-coupling protocol. These alkynes underwent zirconium-mediated coupling to yield zirconacycles that afford new tetraaryl-1,3-butadienes upon subsequent protonolysis; these butadienes display deep blue or green emission and represent promising building blocks for light-emitting devices. The presented synthetic pathway allows access to new libraries of molecular light emitters with tunable luminescence and considerable thermal- and photo-stabilities.



INTRODUCTION

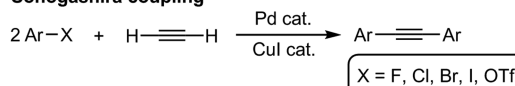
Diarylalkynes are important precursors for the synthesis of olefins,^{1,2} ketones,³ fused organic heterocycles⁴ as well as functional inorganic heterocycles such as luminescent benzo-fused heteroles,⁵ Te/B heterocycles,⁶ π -conjugated systems,⁷ spirocycles,⁸ vinyl cations,⁹ arylalkene polymers,¹⁰ and materials with a broad range of biological activities¹¹ (e.g., 5-azaindoles)¹² and nonlinear optical properties.¹³

In general, the most common route to yield diarylalkynes is Sonogashira coupling: the palladium-catalyzed coupling of aryl or alkenyl halides (or triflates) with terminal alkynes.¹⁴ Recent developments in the Sonogashira methodology include nanoparticle-catalyzed, ligand-free, and/or metal-free coupling, as well as photocatalyzed and microwave-assisted reactions in water.^{14c}

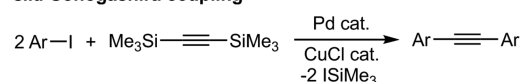
Despite the common use of Sonogashira coupling to form symmetric diarylalkynes, there are some drawbacks including limitations in aryl halide substrate scope when using protected acetylenes¹⁵ and the multistep nature of known protocols, leading to low overall yields. In order to overcome these limitations Lee^{15,16} and others¹⁷ focused attention on the development of decarboxylative alkyne coupling, where propiolic acid is used as an alkyne source (Scheme 1). Other methods of diarylalkyne synthesis (some of which are outlined in Scheme 1) include sila-Sonogashira coupling,¹⁸ Stille coupling,^{8c,19} the use of organoaluminum alkyne²⁰ or alkynylsilanol reagents,²¹ the platinum-catalyzed alkynylation of aryl iodides,²² and Suzuki–Miyaura cross-coupling.²³ In the latter method, Sun's group employed a successful multistep synthesis using boronic acids and thermally unstable acetylene iodides as coupling partners to obtain unsymmetrical alkynes (Scheme 2).^{23b}

Scheme 1. Selected Examples of Diarylalkyne Synthesis

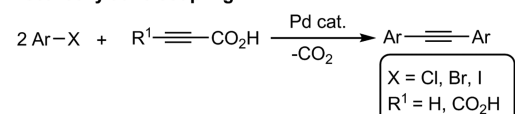
Sonogashira coupling



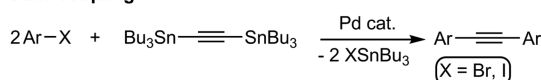
sila-Sonogashira coupling



Decarboxylative coupling



Stille coupling

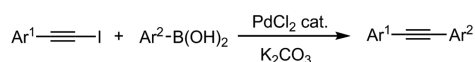


In this paper we report the coupling of the easily prepared diborethyne synthon PinBC \equiv CBPin (**1**)²⁴ with various aryl bromides in a general palladium-catalyzed Suzuki–Miyaura cross-coupling reaction to construct symmetric diarylalkynes in moderate to high yields (Scheme 2). Advantages of this methodology include a timesaving one-pot procedure (i.e., reduction of workup and purification steps compared to the Sonogashira method) and the use of commercially available aryl

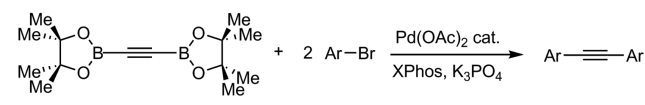
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Scheme 2. Synthesis of Diarylalkynes Using Suzuki–Miyaura Cross-Coupling

Previously reported reaction:



This work:



bromides as substrates. The resulting diarylalkynes can also be used to prepare tetraaryl-substituted 1,3-butadienes that exhibit color tunable luminescence and valuable solid-state emission properties.^{25,26} Accordingly our current study represents an efficient general synthetic methodology for accessing a wide library of luminogens.

RESULTS AND DISCUSSION

Synthesis of Diarylalkynes via Suzuki–Miyaura Coupling. This project began with an evaluation of the stability of the diborylethyne reagent **1**²⁴ to base-induced pinacolboronate (BPIn) cleavage, termed protodeboronation, as this is a common side reaction during Suzuki–Miyaura cross-coupling.²⁷ In order to minimize reaction time, microwave irradiation was applied with compound **1** dissolved in either predried THF or freshly distilled DMF (as these solvents readily absorb microwave irradiation). When DMF solutions of **1** were heated to 100 °C for 20 min, compound **1** was completely converted into the known hydroxide HOBBPin²⁸ (as confirmed by multinuclear NMR spectroscopy), indicating the likely presence of residual water in the DMF. Upon careful examination of the protodeboronated product mixture, the known alkyne HC≡CBPin²⁹ could not be detected, suggesting that the alkyne unit was eliminated as acetylene. In contrast, a THF solution of PinBC≡CBPin (**1**) does not undergo decomposition, even after prolonged heating in the microwave reactor to 140 °C for 40 min; while under the same microwave conditions, **1** in a 3:1 THF/H₂O mixture completely converted into HOBBPin, indicating the key role of water in protodeboronation.

Next we evaluated the effect of added base on the stability of **1** under microwave-assisted reaction conditions (see Table S2

in the Supporting Information). In each trial, compound **1** was dissolved in either THF or DMF (0.12 M solutions), and 6 equiv of oven-dried K₃PO₄ was added. Upon the microwave heating of **1**/K₃PO₄ in THF at 70 °C for 40 min, compound **1** completely decomposed into the bis-boryloxide PinBOBBPin³⁰ and hydroxide HO-BPin; the same reaction carried out in DMF gave only HOBBPin as a boron-containing product. In addition, heating **1**/K₃PO₄ to reflux in THF for 36 h led to partial decomposition of **1** (11% according to ¹H and ¹¹B NMR spectroscopy) into PinBOBBPin. One possible explanation for the formation of protodeboronation products with K₃PO₄ under seemingly nonaqueous conditions is the presence of residual water in the potassium phosphate, despite prior heating at 170 °C for 2 days. When **1** and CsF (2 equiv) were heated in a microwave reactor to 70 °C for 40 min in THF, similarly rapid protodeboronation to yield HOBBPin transpired. Not surprisingly, the use of aqueous potassium carbonate (6 equiv) as a base under the same microwave reaction conditions converted **1** into hydroxide HOBBPin. These trials effectively show that protodeboronation is a reaction that will compete with C–C bond formation during Suzuki–Miyaura cross-coupling, leading to some reduction in yield of the target diarylalkyne (*vide infra*).

We chose 4-bromoisopropylbenzene as a substrate for cross-coupling optimization trials, as the target diarylalkyne (4-¹PrC₆H₄)C≡C(C₆H₄¹Pr-4) (**2**) could only be previously prepared via challenging multistep procedures.³¹ The catalytic system Pd₂(dba)₃/XPhos (dba = dibenzylideneacetone)³² was explored under different conditions, starting from microwave heating at 100 °C for 20 min and up to 140 °C for 40 min in different solvents (Table 1). The best isolated yield of **2** (Scheme 3) was 55% and arose when a Pd₂(dba)₃–XPhos–K₃PO₄ precatalyst/ligand/base system was employed with microwave heating to 140 °C for 40 min in THF. The analogous reactions in DMF or toluene did not yield any product. In the case of DMF, the complete protodeboronation of **1** transpired, while in toluene, no reaction occurred, as toluene is known to be a poor absorber of microwave radiation.³³ Interestingly, use of a THF/H₂O (3:1) solvent combination gave the desired product (4-¹PrC₆H₄)C≡C(C₆H₄¹Pr-4) (**2**) in a 30% isolated yield after purification by column chromatography, while on the other hand a DMF/H₂O (3:1) solvent medium did not lead to the formation of **2**, with only protodeboronation transpiring. Overall the microwave-

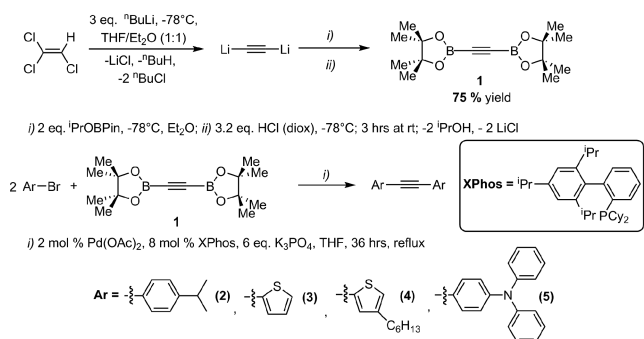
Table 1. Optimization of Reaction Conditions to Synthesize Compound **2**

entry	catalyst, mol % of Pd	ligand, mol %	base, equiv ^a	solvent ^b	temperature (°C)	time (min)	purified yield, %
1	Pd ₂ (dba) ₃ , 2	XPhos, 8	K ₃ PO ₄ , 6	THF	100	20	24
2	Pd ₂ (dba) ₃ , 2	XPhos, 8	K ₃ PO ₄ , 6	DMF	100	20	31
3	Pd ₂ (dba) ₃ , 2	XPhos, 8	K ₃ PO ₄ , 6	THF	100	40	35
4	Pd ₂ (dba) ₃ , 2	XPhos, 8	K ₃ PO ₄ , 6	THF	140	40	55
5	Pd ₂ (dba) ₃ , 2	XPhos, 8	K ₃ PO ₄ , 6	DMF	140	40	0
6	Pd ₂ (dba) ₃ , 2	XPhos, 8	K ₃ PO ₄ , 6	Toluene	140	40	0
7	Pd ₂ (dba) ₃ , 2	XPhos, 8	K ₂ CO ₃ (aq), 6	THF	140	40	0
8	Pd ₂ (dba) ₃ , 2	H ¹ Bu ₃ PBF ₄ , 8	K ₂ CO ₃ (aq), 6	THF	140	40	0
9	Pd ₂ (dba) ₃ , 2	H ¹ Bu ₃ PBF ₄ , 8	K ₂ CO ₃ (aq), 6	DMF	140	40	0
10	Pd ₂ (dba) ₃ , 2	XPhos, 8	K ₃ PO ₄ , 6	THF:H ₂ O = 3:1	140	40	33
11	Pd ₂ (dba) ₃ , 2	XPhos, 8	K ₃ PO ₄ , 6	DMF:H ₂ O = 3:1	140	40	0

^aK₃PO₄ was dried in an oven at 170 °C for 48 h before use; a 2.0 M aqueous solution of K₂CO₃ was freshly prepared and degassed prior to use.

^bTHF was obtained from a Grubbs-type solvent purification system, and DMF was stirred overnight over CaH₂ (5% w/v), filtered, and then freshly distilled from CaSO₄ and stored over molecular sieves.

Scheme 3. Synthesis of the Symmetric Diarylalkynes 2–5



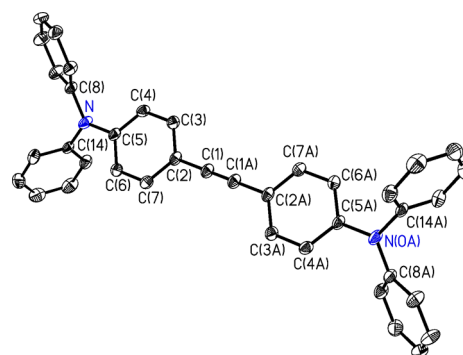
assisted trial reactions summarized in Table 1 helped us to identify a suitable solvent (THF) for future explorations.

In order to effectively scale up the reaction between 4-bromoisopropylbenzene and PinBC \equiv CBPin (**1**), conventional heating in refluxing THF for 36 h was applied with different catalyst/base combinations examined. Specifically we explored Pd catalysts that were commonly used in Suzuki–Miyaura cross-coupling while using 6 equiv of K₃PO₄ base in relation to **1**.^{34a} The Pd(OAc)₂/XPhos (1:4 ratio; 2 mol % of Pd) mixture afforded pure **2** in a 40% isolated yield, which is comparable to the yield obtained with the Pd₂(dba)₃/XPhos combination mentioned above (35% isolated yield of **2**; 2 mol % of Pd). However, the use of 2 mol % of Pd(PPh₃)₄ as a catalyst gave **2** in a much lower isolated yield of 20% (Table 2). In addition, the Pd(OAc)₂/XPhos catalyst combination when mixed with 2 equiv of CsF relative to **1** in THF afforded the target alkyne **2** in an isolated yield of 40%.^{34b} In order to facilitate the handling of the reagents, we chose to use the air-stable precatalyst Pd(OAc)₂ in future coupling reactions instead of the air-sensitive Pd₂(dba)₃. To investigate the effect of the Pd(OAc)₂/XPhos/K₃PO₄ mixture on the stability of **1**, a THF solution of **1** in the presence of Pd(OAc)₂/XPhos (1:4 ratio; 2 mol % of Pd) and K₃PO₄ (6 equiv) was heated to reflux for 36 h, leading to partial decomposition (ca. 40%) of **1** into PinBOBPIn; this represents a slight increase in protodeboronation when compared to heating **1** with 6 equiv of K₃PO₄ in the absence of Pd(OAc)₂/XPhos (only 11% decomposition occurred).

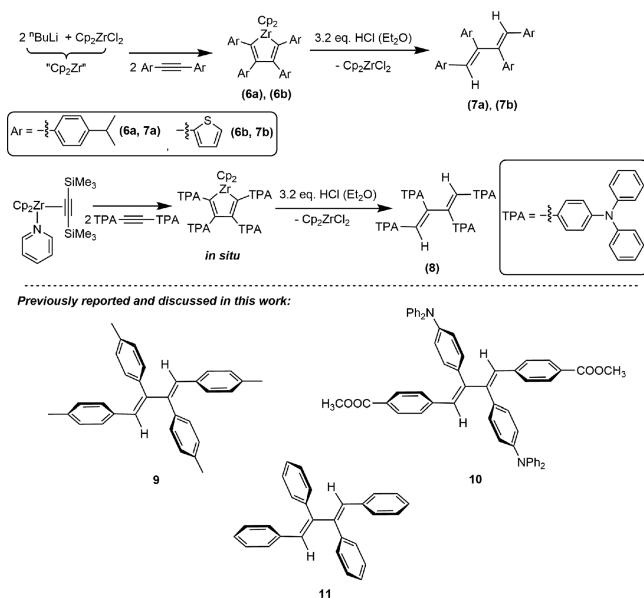
To further investigate the developed synthetic procedure, the thiophene-substituted acetylenes **3** and **4** were prepared according to the conditions presented in Scheme 3 and in Table S5 of the Supporting Information. After slight variations in the catalytic loadings and reaction times, we found that a reaction mixture with a 1:4 ratio of the Pd(OAc)₂ precatalyst to the XPhos ligand in THF that is refluxed for 36 h gave

repeatedly the best isolated yields of analytically pure bis(thienyl)alkynes **3** and **4** (40% and 51% yield, respectively) after column chromatography. We also prepared the symmetric alkyne **5** containing capping triphenylamine (TPA) groups due to the use of TPA units to achieve two-photon absorption and enhanced hole transport properties in optoelectronics.³⁵ The diarylalkynes **2**–**5** were obtained as very pure materials in ca. 30–50% yield after column chromatography; however one can rapidly obtain alkynes **2**, **3**, and **5** in >90–95% purity (according to ¹H NMR) by simply washing the crude alkynes **2**, **3**, and **5** with Et₂O, leading to enhanced isolated yields of 73% (**2**), 40% (**3**), and 60% (**5**).

The structures of alkynes **2** and **5** were confirmed by single-crystal X-ray crystallography (Figures S1 and 1, respectively)



Scheme 4. Synthetic Route to the 1,3-Butadienes 7a/b and Structures of the Known Analogues 9–11



(made from $\text{Cp}_2\text{ZrCl}_2/2^n\text{BuLi}$)^{36a} in THF. The new zirconacycle **6a** was isolated as an air- and moisture-sensitive red solid in a high yield of 90%, and its structure was determined by single-crystal X-ray crystallography (Figure 2). The average

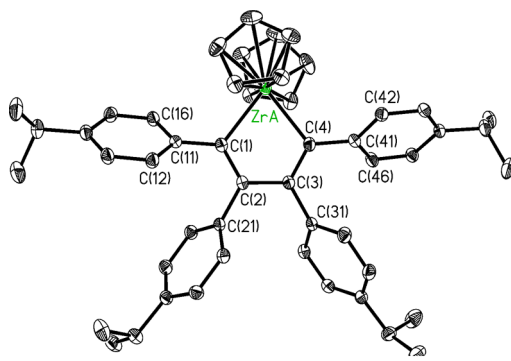


Figure 2. Thermal ellipsoid plot (30% probability) of compound **6a** with hydrogen atoms omitted for clarity; only one molecule of the two in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg) with metrical parameters for the second molecule in the asymmetric unit are listed in square brackets: Zr–C(1) 2.269(2) [2.259(3)], Zr–C(4) 2.267(3) [2.259(3)], C(1)–C(2) 1.363(4) [1.369(4)], C(2)–C(3) 1.489(3) [1.494(3)], C(3)–C(4) 1.366(3) [1.368(4)]; C(1)–Zr–C(4) 77.50(9) [78.27(9)].

Zr–C bond lengths in the five-membered ZrC_4 ring in **6a** are 2.264(4) Å and in accordance with the reported Zr–C bond lengths in pinacolboronate-functionalized zirconacycles.³⁷ The cumyl groups adjacent to the Cp_2Zr unit are twisted from the five-membered zirconacycle core by 55.80(6)° and 58.25(8)°, while the remaining cumyl-based rings are also canted by 55.80(8)° and 54.90(9)° to yield an overall propeller arrangement of the four cumyl groups in **6a**.

Conversion of the zirconacycles **6a** and **6b** into the target 1,3-butadienes **7a** and **7b** with exclusive cis–trans–cis geometries of the appended aryl groups was readily accomplished by adding an excess of HCl in Et_2O (Scheme 4). The Cp_2ZrCl_2 byproduct was effectively removed by filtration of a CH_2Cl_2 /

hexanes solution of the reaction products through a silica gel plug. Compound **7a** was obtained as a white solid (57% yield) after further washing with hexanes, while compound **7b** was isolated as a yellow solid (40% yield) after washing the crude material with cold (−35 °C) Et_2O . Both the cumyl-substituted butadiene **7a** and the thiophene-capped analogue **7b** yielded crystals of suitable quality for X-ray analysis, and their respective structures are found as Figures 3 and 4. As in the

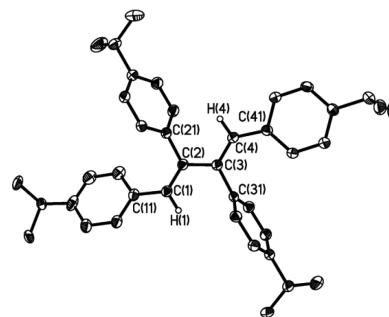


Figure 3. Thermal ellipsoid plot (30% probability) of compound **7a** with selected hydrogen atoms omitted for clarity; remaining hydrogen atoms presented with arbitrarily small thermal parameters. Only the major orientation of the disordered isopropyl groups is shown. Selected bond lengths (Å) and angles (deg): C(1)–C(2) 1.347(3), C(2)–C(3) 1.477(3), C(3)–C(4) 1.347(3); C(2)–C(3)–C(4) 121.07(17), C(1)–C(2)–C(3) 121.70(17).

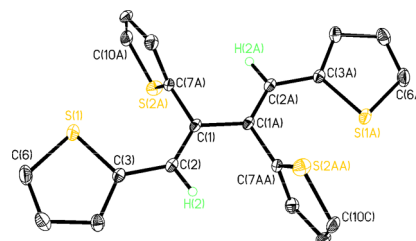


Figure 4. Thermal ellipsoid plot (30% probability) of compound **7b** with selected hydrogen atoms omitted for clarity; remaining hydrogen atoms presented with arbitrarily small thermal parameters. Only the major orientation of the disordered thienyl groups is shown. A crystallographic inversion center (1/2, 0, 1/2) lies at the midpoint of the C(1)–C(1A) bond. Selected bond lengths (Å) and angles (deg): C(1)–C(1A) 1.477(2), C(1)–C(2) 1.351(2), C(2)–C(3) 1.4489(19); C(2)–C(1)–C(1A) 121.31(15), C(1)–C(1A)–C(2A) 121.31(15).

previously characterized tetratolyl-1,3-butadiene **9** and tetraphenyl-1,3-butadiene **11** (Scheme 4),^{26b,c} one of the four aryl rings in compound **7a** (containing C(41), Figure 3) is nearly coplanar with the butadiene core (dihedral angle of 4°), while the remaining rings are twisted from the diene unit by 34.9°, 67°, and 87.5°. Due to the significant twisting of the aryl groups and the presence of sterically encumbered isopropyl groups in **7a**, there is a lack of substantial intermolecular π – π stacking; however significant intermolecular aryl–(H–C)aryl contacts are present (as short as 2.46 Å). In the case of **7b**, the two terminally positioned thienyl groups are only slightly twisted from the butadiene core by 8.8°, while the two remaining thienyl rings are arranged in a nearly perpendicular fashion.

Although the TPA-functionalized butadiene **8** could be obtained using the zirconium source “ Cp_2Zr ” (generated from $\text{Cp}_2\text{ZrCl}_2/2^n\text{BuLi}$ *in situ*), it could also be obtained via a slightly different one-pot procedure starting from the thermally stable

and isolable Cp_2Zr source $\text{Cp}_2\text{Zr}(\text{pyridine})(\text{Me}_3\text{SiCCSiMe}_3)^{36b}$ (Scheme 4). Specifically, $\text{Cp}_2\text{Zr}(\text{pyridine})(\text{Me}_3\text{SiCCSiMe}_3)$ and 2 equiv of $(\text{TPA})\text{C}\equiv\text{C}(\text{TPA})$ **5** were combined in THF to yield a red solution containing the zirconacycle $\text{Cp}_2\text{ZrC}_4(\text{TPA})_4$, which was reacted *in situ* with an excess of HCl to give crude **8** as an orange solid. The resulting product contained Cp_2ZrCl_2 byproduct as well as unreacted **5**; thus additional purification by multiple washes with cold (-30°C) Et_2O , followed by washing with acetone at room temperature, was required to afford pure **8** as a bright yellow solid in a 26% yield. Unfortunately, we have not been able to obtain crystals of **8** of suitable quality for single-crystal X-ray crystallographic analysis.

Optical Properties of the Tetraaryl-1,3-butadienes 7a, 7b, and 8. Tetraarylbutadienes are an emerging class of solid-state emitters with high photoluminescence quantum yield; thus the optical properties of **7a**, **7b**, and **8** were studied in more detail. Compounds **7a** and **7b** undergo a drastic change from a nonemissive state in THF solution to highly emissive aggregated states in THF/ H_2O mixtures when the water content exceeded 60% v/v and 80% v/v, respectively; this effect is termed aggregation-induced emission²⁵ and was previously observed for butadienes **9–11**.²⁶ The fluorescence emission spectra of **7a/b** in THF/ H_2O are presented in Figures 5 and

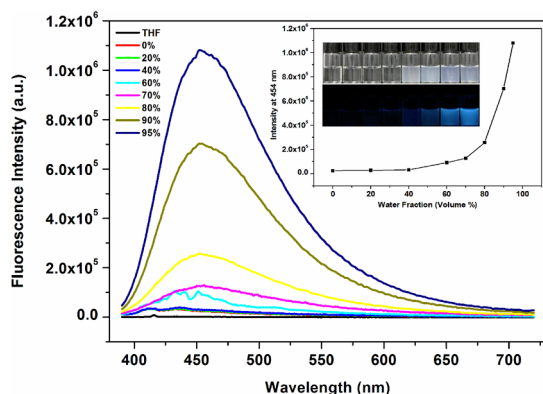


Figure 5. Photoluminescence spectra of **7a** in different THF/water ratios (listed as % water content). Inset: Emission intensity of **7a** as the THF/water ratio is altered. Inset photo: Aggregates under UV light ($\lambda_{\text{ex}} = 365\text{ nm}$); $[\text{7a}] = 10^{-4}\text{ M}$.

S34 in the Supporting Information. In addition, compound **7a** emits a bright blue color in the solid state ($\lambda_{\text{emis}} = 426$ and 463 nm) due to the restricted rotation of the peripheral cumyl groups (Figure S32). As a comparison, bright green photoluminescence ($\lambda_{\text{emis}} = 506\text{ nm}$) is noted in the solid state for **7b** with a spectral tail that extends to ca. 650 nm (Figure S33).

Given the emissive nature of unsaturated compounds bearing TPA substituents, we decided to investigate the luminescence of the alkyne **5** and its 1,3-butadiene derivative **8**. In agreement with previously reported emission data for **5** in CHCl_3 ,^{35b} alkyne **5** displays blue emission in THF when irradiated at 267 and 322 nm ($\lambda_{\text{emis}} = 413\text{ nm}$, $\Phi_{\text{absolute}} = 79.7\%$; Figure S31); however this emission maxima is slightly blue-shifted when compared to that in CHCl_3 , where $\lambda_{\text{emis}} = \text{ca. } 430\text{ nm}$. The relative quantum yield of **5** (vs quinine sulfate in $1.0\text{ N H}_2\text{SO}_4$) is lower within predicted error³⁸ than its absolute quantum yield and is presented in the Experimental Section. The 1,3-butadiene analogue **8** shows a change of luminescence color upon aggregation, which one could conceivably take advantage

of for sensing applications.^{26c} When **8** is dissolved in THF, blue-green emission is observed ($\lambda_{\text{emis}} = 472\text{ nm}$, $\Phi_{\text{absolute}} = 34.6\%$, $\tau = 2.1\text{ ns}$); however in the film state there is a substantial red-shift in λ_{emis} to 516 nm , corresponding to bright green emission (Figure 6). As a comparison, the relative

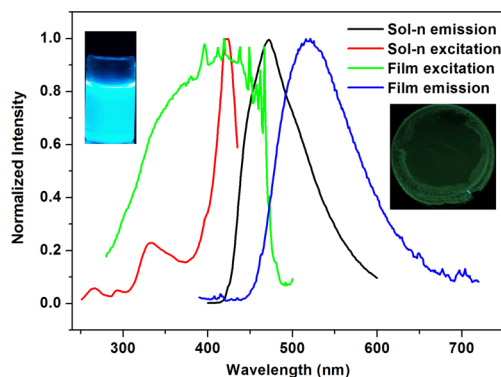


Figure 6. Normalized PL excitation and emission spectra of **8** with $\lambda_{\text{ex}} = 423\text{ nm}$ in THF and $\lambda_{\text{ex}} = 423\text{ nm}$ in the film state.

quantum yield of the TPA-containing butadiene **10** (Scheme 4) in THF ($\Phi = 4.7\%$; $\lambda_{\text{emis}} = 545\text{ nm}$) is about 7-fold lower as in **8**; thus the added TPA units and overall steric bulk in **8** appear to hinder nonradiative decay pathways.^{26a} Similarly to **5** and **10**,^{26a} the UV/vis spectrum of **8** shows absorption peaks at 305 and 380 nm in THF (Figure S30); however in line with the dramatic changes in emission data in the solid state, the longer wavelength absorption is red-shifted by ca. 30 nm to 410 nm ; thus aggregation triggers enhanced conjugation within **8**. The aggregation behavior of compound **8** is very different compared to the butadienes **7a/b** and **9–11**, which do not show a change in photoluminescence color upon aggregation, but rather only an enhancement of emission intensity.²⁶ Under UV irradiation **8** undergoes a change from blue emission in pure THF ($\lambda_{\text{emis}} = 472\text{ nm}$) to green ($\lambda_{\text{emis}} = 505\text{ nm}$) when the water composition exceeds 60% v/v (Figure 7), in line with aggregation promoting restricted intramolecular motion and enhanced conjugation in **8**.

The solid-state emission spectra for the butadienes **7a,b** and **8** were recorded from amorphous films (with amorphous

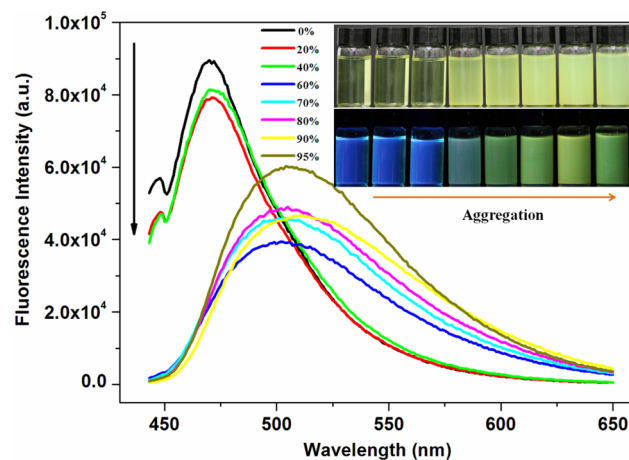


Figure 7. Photoluminescence spectra of **8** in different THF/water ratios (listed as % water content). Inset: Aggregates under UV light ($\lambda_{\text{ex}} = 365\text{ nm}$); $[\text{8}] = 10^{-4}\text{ M}$.

character confirmed by X-ray powder diffraction; Figure S35). Compounds **5**, **7a**, **7b**, and **8** all show fluorescence in the solid state according to the lifetimes found: 2.4, 1.0, 1.2, and 2.1 ns, respectively. The 1,3-butadiene analogue **7a** has the highest absolute quantum yield of 24.8% in the solid state, while the thiophene-capped analogue **7b** and alkyne **5** have similarly low quantum yields of 1.5% and 1.7%. Even though in solution the quantum yield of **8** was higher than that of **10** ($\Phi = 34.6\%$ versus 4.7%), in the solid state **8** has quantum yield of 10.7%, while the previously reported TPA-substituted butadiene **10** has a solid-state photoluminescence quantum yield of 40.1%.^{26c,39} Given the lack of X-ray data for **8**, it is difficult to provide a convincing reason for the reduced fluorescence efficiency of **8** in the solid state.

Photooxidation and Thermal Stability of Functionalized Tetraaryl-1,3-butadienes. To determine how the incorporation of cumyl, thienyl, or triphenylamine groups within a butadiene framework affects the photostability, thin amorphous films of **7a/b** and **8** were irradiated under air. In each photostability trial, 30 μL of a 2.0×10^{-3} M THF solution of the butadiene was drop-casted onto a glass slide, and each experiment was conducted in triplicate under aerobic conditions (see Figures 8, S36, and S37). To the best of our

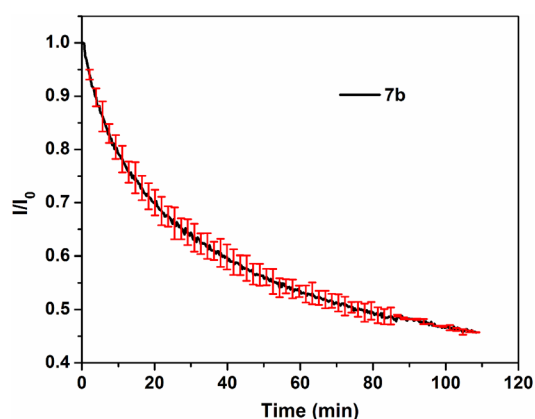


Figure 8. Time dependence of the fluorescence emission intensity of a drop-cast thin film of **7b** (from 30 μL of a 2.0×10^{-3} M THF solution) upon exposure to a 65 W xenon lamp in air. Film distance from lamp was 130 cm.

knowledge, this is the first example of such a study for tetraaryl-substituted 1,3-butadienes and helps identify candidates for the development of LEDs that work without substantial encapsulation.⁴⁰ After drop-casting, the resulting amorphous films of **7a**, **7b**, and **8** were irradiated in air with a 65 W xenon lamp found within our fluorimeter. The resulting I/I_0 ratios were derived from the recorded photoluminescence intensity at the emission wavelength, λ_{max} . The cumyl (4-isopropylbenzene)-substituted butadiene **7a** showed rapid degradation with 50% retention of emission intensity ($I/I_0 = 0.50$) after 23 min of exposure (Figure S36); the TPA-functionalized butadiene **8** retains half of the initial photoluminescence (PL) intensity after 16 min of exposure (Figure S37). The thiophene-appended butadiene **7b** shows considerably enhanced photostability⁴¹ relative to **7a** and **8**, with a 50% reduction in PL after 75 min of sustained exposure to the xenon lamp (Figure 8). A decrease of the emission intensity due to degradation of the butadienes was also verified by UV/vis spectroscopy (Figures S38–S40).

Thermal stability is another important parameter to consider when selecting emitters for full-color displays. The onset of thermal decomposition (5% weight loss, T_d) of compounds **7a/b** and **8** was evaluated under nitrogen using thermal gravimetric analysis (Figure 9). The TPA-functionalized butadiene **8** has

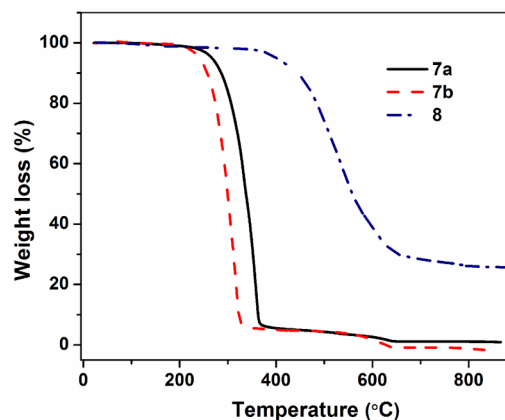


Figure 9. TGA thermograms of **7a**, **7b**, and **8** measured under N_2 (scan rate = 10 $^\circ\text{C}/\text{min}$).

the highest thermal stability ($T_d = 401$ $^\circ\text{C}$) in the series, followed by the cumyl-substituted butadiene **7a** ($T_d = 267$ $^\circ\text{C}$) and thienyl analogue **7b** ($T_d = 241$ $^\circ\text{C}$). This trend is mirrored by the precursor diarylalkynes **2–5** (Figure S41), albeit with lower thermal stabilities. The most thermally stable diarylalkyne is (TPA) $\text{C}\equiv\text{C}$ (TPA) (**5**), with a T_d of 206 $^\circ\text{C}$, followed by the cumyl-substituted alkyne **2** ($T_d = 186$ $^\circ\text{C}$) and the thiophene-appended alkyne **3** ($T_d = 118$ $^\circ\text{C}$). Surprised by the low apparent decomposition temperature of (2-thienyl) $\text{C}\equiv\text{C}$ (2-thienyl) (**3**), we measured its melting point in a sealed capillary tube under a nitrogen atmosphere and found that this compound melts at 97–100 $^\circ\text{C}$ without any decomposition; notable discoloration started at 175 $^\circ\text{C}$, and the melt became dark brown at 230 $^\circ\text{C}$. Based on the DSC measurements under a nitrogen atmosphere, the alkyne **3** melts at 97–100 $^\circ\text{C}$ (in agreement with melting point data) and decomposes at 179 $^\circ\text{C}$; thus 118 $^\circ\text{C}$ is the temperature at which 5% weight loss is most likely due to the evaporation of the alkyne. Compound **3** was also heated in refluxing toluene (ca. 110 $^\circ\text{C}$) for 24 h with no sign of decomposition; such a result is important, as this alkyne is being increasingly used as a reagent in the chemical community, for instance in the preparation of conducting and fluorescent polymers.³³

Compounds **7a/b** also yielded dramatic weight losses (up to 95%) when subjected to TGA under N_2 (Figure 9). Upon heating from ambient temperature to 800 $^\circ\text{C}$, the onset of thermal decomposition/weight loss for **7a/b** and **8** was found at 230, 271, and 308 $^\circ\text{C}$. The melting points of these species were extracted from DSC data and afforded values of 209, 218, and 274 $^\circ\text{C}$, respectively (Figures S45–S47), in agreement with those measured in sealed capillary tubes. Compound **7a** also showed a crystallization temperature (T_c) of 130 $^\circ\text{C}$, which emerged upon cooling of the melt. To test possible decomposition, compounds **7a/b** and **8** were subjected to repeated heating and cooling cycles in the DSC to temperatures ca. 10 $^\circ\text{C}$ above noticeable melting events; the weight loss after these measurements was negligible (<2%), excluding the evaporation of butadienes **7a/b** and **8** during heating. It was found that the cumyl-capped butadiene **7a** has a stable melt, as

noted by reoccurring melting/recrystallization after the first cycle. In contrast, recrystallization and melting were not observed after the first heating for compounds **7b** and **8**, thus confirming their decomposition upon melting. Thus, the weight loss in **7a** noted during TGA could be due to evaporation (which is rapid above 230 °C), while in **7b** decomposition occurs upon melting.

CONCLUSIONS

We have developed a general synthetic protocol to yield diarylalkynes and functionalized tetraaryl-1,3-butadienes via sequential Suzuki–Miyaura and zirconium-mediated alkyne coupling. Altering the nature of the peripheral substituents appended to the butadiene unit leads to blue or green photoluminescence in the solid state. Future work will involve incorporating these emissive units into polymeric structures for the fabrication of mechanically robust LEDs.

EXPERIMENTAL SECTION

Materials and Instrumentation. All reactions were performed using standard Schlenk and glovebox (MBraun) techniques under a nitrogen atmosphere. Solvents were all dried and degassed using a Grubbs-type solvent purification system⁴² manufactured by Innovative Technology, Inc., and stored under an atmosphere of nitrogen prior to use. 4-Bromoisopropylbenzene was obtained from TCI America, palladium(II) diacetate and zirconocene dichloride were from Strem Chemicals Inc., 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was from Oakwood Chemicals, and pyridine was from Caledon Laboratory Chemicals; all other chemicals were obtained from Aldrich. Commercially obtained chemicals were used as received except for pyridine (pyr), which was freshly distilled under nitrogen from potassium hydroxide.⁴³ Bis(cyclopentadienyl)zirconium(2,3,4,5-tetra-(2-thienyl)methanide) ($\text{Cp}_2\text{ZrC}_4\text{T}_4$),³² $\text{Cp}_2\text{Zr}(\text{pyr})(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)$,⁴⁴ 2-bromo-3-hexylthiophene,⁴⁵ and 4-bromotriphenylamine⁴⁶ were prepared according to literature procedures. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were recorded on a Varian DD2MR-400 spectrometer and referenced externally to SiMe_4 (^1H , $^{13}\text{C}\{^1\text{H}\}$) and $\text{F}_3\text{B}\cdot\text{OEt}_2$ ($^{11}\text{B}\{^1\text{H}\}$). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Mass spectrometry were performed using a MS-50G system (Kratos Analytical). Melting points were obtained in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected. UV/vis measurements were recorded using a Varian Cary 300 Scan spectrophotometer. The fluorescence measurements were conducted on a Photon Technology International (PTI) MP1 fluorescence system. All relative solution quantum yields were measured in comparison to quinine sulfate in 1 N H_2SO_4 as a standard, assuming a quantum yield of 0.55.^{38a} Photoluminescence lifetimes were measured on a time-correlated single-photon-counting fluorescence spectrometer (Edinburgh Instruments FLS920) using an EPL-375 ps pulsed diode laser with vertical polarization (70.3 ps pulse width) as an excitation source; absolute quantum yields were measured with an integrating sphere system within the same fluorescence spectrometer. The X-ray powder diffraction patterns were collected on an Inel diffractometer equipped with a curved position-sensitive detector (CPS 120) and a $\text{Cu K}\alpha_1$ radiation source. Thermogravimetric analysis was performed under a nitrogen atmosphere on a PerkinElmer Pyris 1 TGA. Differential scanning calorimetry measurements were conducted under a nitrogen atmosphere on a PerkinElmer Pyris 1 DSC. Microwave reactions were performed using a Biotage Initiator Classic microwave reactor (Biotage, LLC, Charlotte, NC, USA). Photobleaching experiments on films were performed with a PTI MP1 fluorescence system (xenon lamp, 65 W).

Synthesis of 1,2-Bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)ethyne (1). This compound was synthesized according to a modification of a known procedure.²⁴ To a 100 mL 1:1 mixture of THF and Et_2O at -78°C was added a solution of $^n\text{BuLi}$ (2.5 M in

hexanes, 75 mmol). Then 2.25 mL (25 mmol) of trichloroethylene in 25 mL of Et_2O was added dropwise over 15 min with stirring. After the addition was completed, the cooling bath was removed immediately and the resulting pale yellow mixture was stirred overnight to give a white slurry. The mixture containing dithioacetylide was then transferred via cannula to a precooled (-78°C) solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10 mL, 49 mmol) in Et_2O (100 mL), followed by stirring at -78°C for 4 h. Next the mixture was warmed to room temperature and stirred for 4 h. The reaction mixture was then cooled to -78°C , 20 mL of HCl (4.0 M in dioxane, 80 mmol) was added, and the flask was stirred for 3 h at room temperature. The LiCl precipitate was allowed to settle, and the supernatant was filtered through a pad of Celite. The volatiles were then removed from the filtrate under reduced pressure to give **1** as a brown semisolid, which was washed with cold pentane (2×10 mL; -30°C) to give **1** as an air-stable, light beige powder (5.195 g, 75%). The corresponding ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral data in C_6D_6 matched those reported previously by the Therien group.²⁴ ^1H NMR (400 MHz, CDCl_3): δ 1.25 (s, 24H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 84.7 ($\text{C}(\text{CH}_3)_2$), 24.6 (CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3): δ 23.3 (br).

Synthesis of 1,2-Bis(4-isopropylphenyl)ethyne (2). Compound **1** (1.00 g, 3.60 mmol), 4-bromoisopropylbenzene (1.09 mL, 7.20 mmol), K_3PO_4 (4.58 g, 21.6 mmol), palladium(II) diacetate (0.016 g, 0.072 mmol), and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (0.137 g, 0.288 mmol) were mixed in a 100 mL flask under N_2 . Degassed THF (20 mL) was then added, and the mixture was stirred for 30 min at room temperature (for catalyst activation).⁴⁷ The flask was then immersed in a preheated oil bath, and the solvent was refluxed for 36 h. Afterward the reaction mixture was cooled to room temperature, poured into 100 mL of water, and extracted with 30 mL of chloroform. The organic layer was washed with 100 mL of water and 2×100 mL of brine. The aqueous fractions were combined and extracted with 20 mL of chloroform, and the organic layer was washed with 2×100 mL of brine. Then all combined organic fractions were dried over MgSO_4 . The solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, ethyl acetate:hexanes = 1:20, R_f = 0.74) to give **2** as a light yellow solid (0.417 g, 44%). X-ray quality colorless crystals were obtained upon recrystallization from ethyl acetate/hexanes at room temperature. In addition, the crude mixture can also be purified by washing with cold (-30°C) diethyl ether (2×4 mL) to yield **2** as a pale brown solid (1.003 g of **1** gives 0.687 g of **2**, 73% yield, ca. 95% purity; see Figures S7 and S8). The corresponding ^1H NMR spectral data matched those reported previously in the literature.³¹ TGA: T_{dec} = 186 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.46 (d, $^3J_{\text{HH}}$ = 7.9 Hz, 4H, ArH), 7.21 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 4H, ArH), 2.92 (sept, $^3J_{\text{HH}}$ = 6.9 Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 12H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 149.1, 131.6, 126.5, 120.9 (Ar-C), 88.9 ($-\text{C}\equiv\text{C}-$), 34.1 ($\text{CH}(\text{CH}_3)_2$), 23.9 (CH_3). HR-MS (EI): m/z 262.1721; $\text{C}_{20}\text{H}_{22}$ calcd 262.1722. Anal. Calcd (%) for $\text{C}_{20}\text{H}_{22}$: C, 91.55; H, 8.45. Found: C, 90.73; H, 8.54.

Synthesis of 1,2-Bis(thiophen-2-yl)ethyne (3). In a 100 mL flask, compound **1** (1.00 g, 3.60 mmol), 2-bromothiophene (731 μL , 7.56 mmol), K_3PO_4 (4.58 g, 21.6 mmol), palladium(II) diacetate (0.016 g, 0.072 mmol), and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (0.137 g, 0.288 mmol) were mixed. Degassed THF (20 mL) was then added, and the mixture was stirred for 30 min at room temperature (for catalyst activation).⁴⁷ Then the flask was inserted in a preheated oil bath, and the solvent was refluxed for 36 h. Afterward the reaction mixture was cooled to room temperature, poured into 100 mL of water, and extracted with 30 mL of chloroform. The organic layer was washed with 100 mL of water and 2×100 mL of brine. The aqueous fractions were combined and extracted with 20 mL of chloroform, and the organic fractions were washed with 2×100 mL of brine. Then all combined organic fractions were dried over MgSO_4 . The solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, hexanes, R_f = 0.35) to give **3** as a pale yellow solid (0.275 g, 40%). In addition, the crude residue can also be purified by washing with cold (-30°C) diethyl

ether (2 × 4 mL) to yield **3** as a dark brown solid (0.999 g of **1** gives 0.274 g of **3**, 40% yield, ca. 95% purity; Figures S8 and S9). The corresponding ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral data matched those reported previously in the literature.^{15,48} TGA: $T_{\text{dec}} = 179^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.31 (dd, $^3J_{\text{HH}} = 5.1$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, 2H, ThienylH), 7.29 (dd, $^3J_{\text{HH}} = 3.7$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 2H, ThienylH), 7.02 (dd, $^3J_{\text{HH}} = 5.1$ Hz, $^4J_{\text{HH}} = 3.7$ Hz, 2H, ThienylH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 132.1, 127.6, 127.2, 122.9 (Thienyl-C), 86.3 ($-\text{C}\equiv\text{C}-$). HR-MS (EI): m/z 189.9915; $\text{C}_{10}\text{H}_6\text{S}_2$ calcd 189.9911. Anal. Calcd (%) for $\text{C}_{10}\text{H}_6\text{S}_2$: C, 63.12; H, 3.18; S, 33.70. Found: C, 63.28; H, 3.13; S, 33.64.

Synthesis of 1,2-Bis(3-hexyl-2-thienyl)ethyne (4). Compound **1** (1.013 g, 3.64 mmol), 2-bromo-3-hexylthiophene (1.892 g, 7.65 mmol), K_3PO_4 (4.642 g, 21.8 mmol), palladium(II) diacetate (0.016 g, 0.073 mmol), and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (0.139 g, 0.292 mmol) were mixed in a 100 mL flask under N_2 . Degassed THF (20 mL) was then added, and the mixture was stirred for 30 min at room temperature (for catalyst activation)⁴⁷ and then heated to reflux for 36 h. Afterward the reaction mixture was cooled to room temperature, poured into 100 mL of water, and extracted with 30 mL of chloroform. The organic layer was washed with 100 mL of water and 2 × 100 mL of brine. The aqueous fractions were combined and extracted with 20 mL of chloroform, and the CHCl_3 layer was washed with 2 × 100 mL of brine. Then all combined organic fractions were dried over MgSO_4 . The solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, petroleum ether, $R_f = 0.62$) to give **4** as a pale yellow oil (0.667 g, 51%). The corresponding ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral data matched those reported previously in the literature.^{33,49} ^1H NMR (400 MHz, CDCl_3): δ 7.20 (d, $^3J_{\text{HH}} = 5.2$ Hz, 2H, ThienylH), 6.91 (d, $^3J_{\text{HH}} = 5.2$ Hz, 2H, ThienylH), 2.78 (t, $^3J_{\text{HH}} = 7.7$ Hz, 4H, Thienyl- CH_2), 1.66–1.72 (m, 4H, Thienyl- $\text{CH}_2(\text{CH}_2)_4\text{-CH}_3$), 1.33–1.42 (m, 12H, Thienyl- $\text{CH}_2(\text{CH}_2)_4\text{-CH}_3$), 0.92 (t, $^3J_{\text{HH}} = 7.1$ Hz, 6H, Thienyl- $(\text{CH}_2)_5\text{-CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 147.6, 128.3, 126.1, 118.4 (Thienyl-C), 88.0 ($-\text{C}\equiv\text{C}-$), 31.7, 30.4, 29.7, 29.1, 22.7 (Thienyl- $(\text{CH}_2)_5\text{-CH}_3$), 14.1 (Thienyl- $(\text{CH}_2)_5\text{-CH}_3$). HR-MS (EI): m/z 358.1785; $\text{C}_{22}\text{H}_{30}\text{S}_2$ calcd 358.1789. Anal. Calcd (%) for $\text{C}_{22}\text{H}_{30}\text{S}_2$: C, 73.69; H, 8.43; S, 17.88. Found: C, 73.92; H, 8.39; S, 17.48.

Synthesis of 1,2-Bis(triphenylamine)ethyne (5). In a 100 mL flask, compound **1** (1.015 g, 3.65 mmol), 2-bromo-3-hexylthiophene (2.412 g, 7.44 mmol), K_3PO_4 (4.737 g, 22.3 mmol), palladium(II) diacetate (0.017 g, 0.074 mmol), and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (0.142 g, 0.298 mmol) were mixed. Degassed THF (20 mL) was then added, and the mixture was stirred for 30 min at room temperature (for catalyst activation)⁴⁷ and then heated to reflux for 36 h. Afterward the reaction mixture was cooled to room temperature, poured into 100 mL of water, and extracted with 30 mL of chloroform. The organic layer was washed with 100 mL of water and 2 × 100 mL of brine. The aqueous fractions were combined and extracted with 20 mL of chloroform, and the organic layer was washed with 2 × 100 mL of brine. Then all combined organic fractions were dried over MgSO_4 . The solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, hexanes/ $\text{CH}_2\text{Cl}_2 = 8:2$, $R_f = 0.38$) to give **5** as a pale yellow solid (0.572 g, 31%). Slow evaporation of a solution of **5** in 8:2 hexanes/ CH_2Cl_2 at room temperature resulted in the formation of colorless crystals of X-ray quality (0.286 g, 15%). The crude mixture can also be purified by washing with Et_2O (2 × 15 mL) to yield **5** as a light brown solid of ca. 90% purity in 60% yield (1.015 g of **1** gives 1.116 g of **5**; see Figure S17). TGA: $T_{\text{dec}} = 206^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.38 (d, $^3J_{\text{HH}} = 8.6$ Hz, 4H, ArH), 7.29–7.31 (m, 8H, ArH), 7.07–7.14 (m, 12H, ArH), 7.03 (d, $^3J_{\text{HH}} = 8.6$ Hz, 4H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 147.7, 147.3, 132.4, 129.4, 124.9, 123.5, 122.6, 116.7 (Ar-C), 88.9 ($-\text{C}\equiv\text{C}-$). UV/vis (THF): $\lambda_{\text{max}}(\epsilon) = 301$ nm ($4.02 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$) and 369 nm ($6.65 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$). UV/vis (film): $\lambda_{\text{max}} = 312$ and 367 nm. Fluorescence emission (THF) ($\lambda_{\text{ex}} = 267$, 322 nm): $\lambda_{\text{emis}} = 413$ nm. Fluorescence quantum yield: $\Phi = 48\%$, relative to quinine sulfate in 1.0 N H_2SO_4 . Absolute quantum yield (THF): $\Phi = 79.7\%$. Lifetime (1×10^{-5} M solution in THF): $\tau = 1.4$

ns. Fluorescence emission (film) ($\lambda_{\text{ex}} = 380$ nm): $\lambda_{\text{emis}} = 424$ nm. Lifetime (film): $\tau = 2.4$ ns. Absolute quantum yield (film) = 1.7%. The optical data matched those previously reported.^{35b} HR-MS (EI): m/z 512.2239; $\text{C}_{38}\text{H}_{28}\text{N}_2$ calcd 512.2252. Anal. Calcd (%) for $\text{C}_{38}\text{H}_{28}\text{N}_2$: C, 89.03; H, 5.51; N, 5.46. Found: C, 88.27; H, 5.37; N, 5.43.

Synthesis of Bis(cyclopentadienyl)zirconium(2,3,4,5-tetra(4-isopropylphenyl)methanide) (6a). To a solution of Cp_2ZrCl_2 (0.183 g, 0.63 mmol) in THF (10 mL) at -78°C was added dropwise a solution of $^n\text{BuLi}$ (0.49 mL, 2.5 M solution in hexanes, 1.2 mmol). After the reaction mixture was stirred at -78°C for 1 h, a solution of **2** (0.328 g, 1.25 mmol) in THF (10 mL) was added at -78°C . The temperature was allowed to rise to room temperature, and the mixture was stirred for another 24 h. The solvent was removed under reduced pressure, the product was extracted with 15 mL of toluene, and the resulting extract was filtered through Celite. The volatiles were then removed from the filtrate under reduced pressure to give **6** as a red powder (0.420 g, 90%). This compound was recrystallized from hexanes at -35°C to yield red crystals that were of suitable quality for X-ray crystallography. Mp: $119\text{--}124^\circ\text{C}$ (dec). ^1H NMR (400 MHz, C_6D_6): δ 6.95 (two overlapping doublets, 8H, ArH), 6.73 (d, $^3J_{\text{HH}} = 8.1$ Hz, 4H, ArH), 6.71 (d, $^3J_{\text{HH}} = 8.1$ Hz, 4H, ArH), 6.07 (s, 10H, CpH), 2.66 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.50 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.11 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, CH_3), 0.99 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 194.2, 146.3, 144.8, 143.3, 142.9, 139.6, 131.2, 127.8, 125.9, 125.0 (Ar-C), 112.1 (Cp), 33.81, 33.78 ($\text{CH}(\text{CH}_3)_2$), 24.2, 24.0 (CH_3). UV/vis (THF): $\lambda_{\text{max}}(\epsilon) = 374$ nm ($6.78 \times 10^3 \text{ mol}^{-1} \text{ L cm}^{-1}$). HR-MS (MALDI): m/z 744.3271; $\text{C}_{50}\text{H}_{54}\text{Zr}$ calcd 744.3284. Anal. Calcd (%) for $\text{C}_{50}\text{H}_{54}\text{Zr}$: C, 80.48; H, 7.29. Found: C, 79.93; H, 7.50.

Synthesis of cis,cis-1,2,3,4-Tetrakis(4-isopropylbenzene)-1,3-butadiene (7a). To a solution of **6a** (0.421 g, 0.56 mmol) in 15 mL of Et_2O was added a solution of HCl (0.9 mL, 2.0 M solution in Et_2O , 1.8 mmol). The red color of **6a** immediately disappeared to give a yellow slurry. The mixture was stirred for 12 h at room temperature, and then the solvent was removed under vacuum. The residue was dissolved in a 2:1 CH_2Cl_2 /hexanes solvent mixture (5 mL) and filtered through a 1 cm plug of silica gel. The solvent was removed from the filtrate, and the resulting solid (0.220 g, 74%) was washed with hexanes (2 × 5 mL) to yield **7a** as a white solid (0.168 g, 57%). The product was crystallized from hexanes at -35°C to give X-ray quality colorless crystals of **7a**. Mp: $198\text{--}201^\circ\text{C}$. TGA: $T_{\text{dec}} = 267^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.29 (d, $^3J_{\text{HH}} = 8.1$ Hz, 4H, ArH), 7.24 (d, $^3J_{\text{HH}} = 8.1$ Hz, 4H, ArH), 6.89 (d, $^3J_{\text{HH}} = 8.1$ Hz, 4H, ArH), 6.66 (d, $^3J_{\text{HH}} = 8.1$ Hz, 4H, ArH), 6.24 (s, 2H, $=\text{CH}-$), 3.00 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.76 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.35 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, CH_3), 1.16 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 147.8, 147.2, 145.2, 137.6, 135.1, 131.2, 130.2, 129.5, 126.8, 125.9 (Ar-C), 34.0, 33.7 ($\text{CH}(\text{CH}_3)_2$), 24.2, 23.8 (CH_3). UV/vis (THF): $\lambda_{\text{max}}(\epsilon) = 327$ nm ($3.06 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$), 339 nm ($3.49 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$), and 356 nm ($2.38 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$). UV/vis (film): $\lambda_{\text{max}} = 331$, 346, and 367 nm. Fluorescence emission (film) ($\lambda_{\text{ex}} = 380$ nm): $\lambda_{\text{emis}} = 426$ and 463 nm. Lifetime (film): $\tau = 1.0$ ns. Absolute quantum yield (film) = 24.8%. HR-MS (EI): m/z 526.3597; $\text{C}_{40}\text{H}_{46}$ calcd 526.3600. Anal. Calcd (%) for $\text{C}_{40}\text{H}_{46}$: C, 91.20; H, 8.80. Found: C, 91.26; H, 9.01.

Synthesis of cis,cis-1,2,3,4-Tetrakis(2-thienyl)-1,3-butadiene (7b). To a solution of **6b**³² (0.202 g, 0.34 mmol) in 10 mL of THF was added a solution of HCl (0.54 mL, 2.0 M solution in Et_2O , 1.09 mmol). The red color of **6b** immediately disappeared to give a yellow slurry. The mixture was stirred for 12 h at room temperature, and the solvent was removed under vacuum; the pale yellow residue was then dissolved in dichloromethane (5 mL) and filtered through a 1 cm plug of silica gel with a CH_2Cl_2 /hexanes = 2:1 solvent mixture (30 mL). The solvent was removed from the filtrate, and the product was washed with cold (-35°C) Et_2O (5 mL) to yield **7b** as a bright yellow solid (0.051 g, 40%). Mp: $198\text{--}200^\circ\text{C}$. TGA: $T_{\text{dec}} = 241^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.62 (dd, $^3J_{\text{HH}} = 5.1$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, 2H, ThienylH), 7.25 (dd, $^3J_{\text{HH}} = 5.1$ Hz, $^4J_{\text{HH}} = 3.4$ Hz, 2H, ThienylH), 7.13 (dd, $^3J_{\text{HH}} = 5.0$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, 2H, ThienylH), 7.05 (dd, $^3J_{\text{HH}} = 3.4$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, 2H, ThienylH), 6.85 (dd, $^3J_{\text{HH}} = 3.7$ Hz, $^4J_{\text{HH}}$

= 1.3 Hz, 2H, ThienylH), 6.80 (dd, $^3J_{\text{HH}} = 3.6$ Hz, $^4J_{\text{HH}} = 0.7$ Hz, 2H, ThienylH), 6.73 (s, 2H, $=\text{CH}-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 140.9, 137.8, 134.3, 130.0, 129.3, 128.2, 128.1, 128.0, 127.8, 126.2. UV/vis (THF): λ_{max} (ϵ) = 350, 367, and 387 nm (2.65×10^4 , 3.61×10^4 and 2.81×10^4 mol^{-1} L cm^{-1}). UV/vis (film): $\lambda_{\text{max}} = 364$, 384, and 410 nm. Fluorescence emission (film) ($\lambda_{\text{ex}} = 383$ nm): $\lambda_{\text{em}} = 506$ nm. Lifetime (film): $\tau = 1.2$ ns. Absolute quantum yield (film) = 1.5%. HR-MS (EI): m/z 381.9979; $\text{C}_{20}\text{H}_{14}\text{S}_4$ calcd 381.9978. Anal. Calcd (%) for $\text{C}_{20}\text{H}_{14}\text{S}_4$: C, 62.79; H, 3.69; S, 33.52. Found: C, 62.76; H, 3.70; S, 32.98.

Synthesis of cis,cis-1,2,3,4-Tetrakis(4-triphenylamine)-1,3-butadiene (8). Compound 5 (0.316 g, 0.62 mmol) and $\text{Cp}_2\text{Zr}(\text{pyr})(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)^{4+}$ (0.145 g, 0.31 mmol) were dissolved in 10 mL of THF, and the resulting mixture was allowed to stir for 12 h to give a dark red solution. A solution of HCl (0.6 mL, 2.0 M solution in Et_2O , 1.2 mmol) was added followed by stirring for 12 h at room temperature, resulting in an orange mixture. The solvent was removed under reduced pressure, and the residue was washed with cold Et_2O (2×5 mL, -35°C) and then acetone (3×5 mL) to yield 8 as a bright yellow solid (0.083 g, 26%). Mp $> 250^\circ\text{C}$. TGA: $T_{\text{dec}} = 401^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.25–6.99 (m, 48H, ArH), 6.81 (d, $^3J_{\text{HH}} = 8.8$ Hz, 4H, ArH), 6.72 (d, $^3J_{\text{HH}} = 8.8$ Hz, 4H, ArH), 6.32 (s, 2H, $=\text{CH}-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 147.8, 147.5, 146.9, 146.2, 144.1, 134.4, 131.7, 131.3, 130.5, 130.4, 129.3, 124.5, 124.4, 124.3, 123.0, 122.8, 122.5. UV/vis (THF): λ_{max} (ϵ) = 305 and 380 nm (6.68 and 8.88×10^4 mol^{-1} L cm^{-1}). UV/vis (film): $\lambda_{\text{max}} = 310$ and 410 nm. Fluorescence emission (THF) ($\lambda_{\text{ex}} = 423$ nm): $\lambda_{\text{emis}} = 472$ nm. Fluorescence quantum yield: $\Phi = 13\%$, relative to quinine sulfate in 1.0 N H_2SO_4 . Absolute quantum yield (THF): $\Phi = 34.6\%$. Lifetime (1×10^{-5} M solution in THF): $\tau = 2.1$ ns. Fluorescence emission (film) ($\lambda_{\text{ex}} = 420$ nm): $\lambda_{\text{em}} = 516$ nm. Lifetime (film): $\tau = 2.1$ ns. Absolute quantum yield (film) = 10.7%. HR-MS (MALDI): m/z 1026.4656; $\text{C}_{76}\text{H}_{58}\text{N}_4$ calcd 1026.4661. Anal. Calcd (%) for $\text{C}_{76}\text{H}_{58}\text{N}_4$: C, 88.86; H, 5.69; N, 5.45. Found: C, 87.30; H, 5.69; N, 5.24. Despite repeated attempts, combustion analyses gave consistently low values for carbon content. See Figures S24 and S25 in the Supporting Information for copies of the NMR spectra.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo- met.6b00298.

Development of synthetic procedures for diarylalkynes, crystallographic data, ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra, ultraviolet–visible spectroscopy measurements, photoluminescence spectra, aggregation studies, X-ray powder diffraction patterns, photostability studies, thermogravimetric analysis data, and differential scanning calorimetry curves (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

CCDC reference numbers 1472248 (2), 1472249 (5), 1472250 (6a), 1472251 (7a), and 1472252 (7b) contain the supplementary crystallographic data for the X-ray studies reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road,

Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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