Facile Synthesis of Polyaromatic Bisarylethynes Using a Diborylethyne Synthon

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Ethyne-bridged arylene compounds are important classes of chemical structures that have been studied in broad areas of fundamental research as well as applications.^{1–4} The ethyne bridge has a characteristic structural feature that enforces attached aromatic units in linear and coplanar geometry, which plays an important role in efficient intramolecular electronic interaction.^{5,6} Many conjugated oligomers,^{7–9} polymers,^{10,11} and dendrimers¹² that employ the ethyne group as a major connection unit between the aromatic building blocks have been reported. The ethyne bridge exhibits not only such linear rigidity but also structural flexibility that gives rise to the formation of three dimensional helical structures in foldamers^{13,14} or single-walled carbon nanotube–poly(*p*-arylene)ethynylene adduct.^{15,16}

The simplest form of ethyne-bridged arylene compound is bisarylethyne.^{17–23} The energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital ((LUMO) of the individual aryl unit can be reduced significantly by efficient orbital interaction through two sp carbon atoms that segregate each aryl unit with only ~4 Å distance, and thus gives rise to bathochromic shifts of both absorption and emission spectra. For example, an anthracene that absorbs light below 400 nm wavelength region becomes a visible light chromophore when two of them are connected by the ethyne group.^{24,25} More than 5000 cm⁻¹ of bathochromic shift can be achieved by such simple change of chemical structure. And a Q-band absorption of meso-substituted metal porphyrins in the central visible region shifts to the near IR region when two porphyryl units are coupled through an ethyne group.¹ These types of molecules have interesting features of polymorphism,^{25–27} structure-dependent fluorescence,^{25,28} unusually high fluorescence quantum yield,²⁹ intramolecular charge transfer dynamics in the excited state,²⁴ and nonlinear optical property.³⁰ Similar modification with ethene bridge, however, which is often employed in the architecture of conjugated polymer, cannot afford the coplanar geometry of two anthracene units due to the steric hindrance between the anthryl proton in positions 1 and 9 and the ethenyl protons.³¹ Coplanar conjugated geometries possible for the polyphenylenevinylenes or bisarylethenes become cascade structures in the case of bisanthrylethene. Facile synthesis of ethynebridged polyaromatic dimer is thus important for the study

of solar energy conversion,³² sensors,³³ imaging,³⁴ and molecular electronic devices.^{35,36}

A series of bisarylethyne compounds have already been synthesized by different approaches. Nakagawa et al. have synthesized polyaromatic bisarylethynes by means of pyrolytic decomposition of β-ketoalkylidene-triphenylphosphorane.¹⁹ Pd-catalyzed Sonogashira cross-coupling reaction between aryl halide and aryl ethyne is the most widely used method afterwards. Besides its iterative silane protection/deprotection of terminal ethynylenes,²² the production of butadiyne side product is the major obstacle of this method. Alkyne metathesis of aryl propyne was the alternative approach that prevents butadiyne side products; but this method also requires pre-propynylation of aryl halide.³⁷ Moreover, the use of protic polar solvents is not allowed for this method. Recently, a couple of facile one-pot synthetic methods to generate bisarylethynes have been reported. One is the utilization of trimethylsilylacetylene in the presence of PdCl₂(PPh₃)₂/CuI catalyst system with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and H₂O as a base and an additive, respectively.²² Another one is the utilization of propiolic acid or 2-butynedioic acid in the presence of PdCl₂(PPh₃)₂/ dppb catalyst system with DBU as a base.²³ These methods are similar to the Sonogashira reaction but a variety of bisarylethyne compounds can be prepared in single step. However, authors of both works were only interested in making bisarylethynes from simple phenyl-based aromatics.

Recently, the synthesis of poly(*p*-aylrene ethynylene) (PPES) using a new ethyne synthon, 1,2-bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)-ethyne (B2C2), has been reported.³⁸ Pd-catalyzed Suzuki–Miyaura polycondensation reaction between B2C2 and diiodoarene was performed even in the aqueous phase without an inert atmosphere. However, the utilization of B2C2 for the synthesis of bisarylethynes has not been reported yet. Herein, we report the synthesis of series polyaromatic bisarylethyne molecules from the reaction between bromoarenes and B2C2 via Pd-catalyzed Suzuki– Miyaura cross-coupling reaction (Scheme 1).

The establishment of appropriate reaction conditions often requires an extensive screening procedure. Targeting for the polyaromatic bisarylethynes, we chose 9-bromoanthracene as a starting material for the optimization of reaction conditions. Although it is typical to start a screening procedure

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Ar-X +
$$O_{O}^{B} = B_{O}^{O}$$
 $Pd, Base$ Ar $Ar = A$

Scheme 1. Synthesis of bisarylethyne from B2C2 ethyne synthon.

for the selection of a suitable catalyst system, we initially performed test reactions to choose a proper solvent to adjust solvent polarity. With the representative known reaction conditions that utilize $PdCl_2(PPh_3)_2$ and aqueous K_2CO_3 as a catalyst and a base, respectively, we tested the reactions with seven different solvent systems that have broad windows of solvent polarity (Table S1, entries 1-7, Supporting Information). The reactions were carried out at 80 °C until no more progress of the reaction was monitored by thin-layer chromatography. Two days of reaction time was necessary to complete the reaction. Results indicated that the reaction gave higher yields as the polarity of the solvent increased. Nonpolar toluene did not produce the desired 1,2-bis(9-anthryl)ethyne at all. Mildly polar DME and DME/EtOH mixture gave only 16 and 5% yields, respectively. Moderately polar n-BuOH also did not give the product at all. When DMF or DMF/EtOH mixture was used, the product yields increased significantly (48 and 40%, respectively). Addition of EtOH did not improve reaction yield. Interestingly, CH₃CN was not effective for the reaction (0%) in spite of its substantial polarity.

The next parameter that we tried to optimize was the catalyst system (Table S1, entries 7-12). Among six different catalyst species, the best result was obtained when Pd(PPh₃)₄ was used (53%, Table S1, entry 11). The performances of PdCl₂(PPh₃)₂ and Pd(P^tBu₃)₂ follow next that gave 48 and 42% yields, respectively. Thus, we tested the reactions with these catalyst systems with another base of aqueous K₃PO₄. The yields were reduced significantly by the change of the base when PdCl₂(PPh₃)₂ and Pd(P^tBu₃)₂ catalysts were used (24 and 13%, respectively, Table S1, entries 13, 15). However, the reduction of the yield was only minor for $Pd(PPh_3)_4$ (45%, Table S1, entry 14), indicating that $Pd(PPh_3)_4$ is a more versatile catalyst.

The work by Mio et al. suggested that the amount of water is crucial for the optimization of the reaction conditions in the synthesis of bisarylethynes.²² Inspired by their work, we tested the effect of solvent/water ratio (Table S1, entries 11, 16-18). Even in the absence of water, the desired product was formed in 51% yield, which is similar to that obtained by the preliminary reaction conditions with a DMF/water ratio of 20. The reaction yield was further increased to 69% when the ratio was increased to 30 (Table 1, entry 17). However, when the ratio was reduced to 10, the yield was only 43%.

The final parameter for the optimization of the reaction conditions was the reaction temperature (Table S1, entries 11, 19–22). The reaction yields maximized at 80 °C; further increase to 90 °C resulted in a slight reduction of product yield (61%). The final reaction conditions are as follows: to the given amount of B2C2, 3 equiv of arylbromide, 10 mol% of

Table 1. Pd-catalyzed Suzuki-Miyaura cross-coupling reactions of arylbromide with B2C2.^a

Ar–Br	Ar-≡-Ar	Yield ^b
Br		69
Br		73
Br		81
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^{*a*} Reaction conditions: Aryl bromide = 100 mg (3 equiv to B2C2), $B2C2 = 36 \text{ mg}, Pd(PPh_3)_4 = 10 \text{ mol}\%$ to B2C2, base = 1 M K₂CO₃ (6 equiv), solvent = DMF, temperature = $80 \degree C$, reaction

time = 2 days. ^b Isolated yield.

^c Reaction time = 1 day.

Pd(PPh₃)₄, 6 equiv of 1 M K₂CO₃, DMF of 30 times of the volume of the aqueous base at 80 °C for 2 days.

With the optimized reaction conditions at hand, we synthesized three representative polyaromatic bisarylethynes, 1,2bis(9-anthryl)ethyne (1), 1,2-bis(9-phenanthrenyl)ethyne (2), 1,2-bis(1-pyrenyl)ethyne (3) as well as 1,2-bis[(10,20bis[2',6'-bis(3",3"-dimethyl-1"-butyloxy)phenyl]porphinato)zinc(II)-5-yl]ethyne. The results are summarized in Table 1.

In order to expand the reaction protocol for general synthesis of bisarylethynes, we applied the established reaction conditions to a series of aryl halides. However, the product yields of bisarylethynes with simple phenylene-based aryl halides were not as satisfactory as we expected. Therefore we attempted to devise other reaction conditions. As the synthesis of PPES with B2C2 was successful via microwave-assisted Suzuki–Miyaura polycondensation,³⁸ we adopted its reaction conditions with slight modifications. Elaborate screening procedures similar to those performed for the optimization of 1 gave reaction conditions that produced series bisarylethynes in moderate to high yields (Table 2). Aryl iodides that include iodobenzene, 1-iodo-4-methoxybenzene, and 2iodothiophene gave desired bisarylethynes in 90, 86, and 99% yields, respectively. When aryl bromides were used, the product yields were reduced; bromobenzene, 1-bromo-4-methoxybenzene, 1-bromo-4-trifluoromethyl-benzene, and 1-bromonaphthalene gave corresponding bisarylethynes in 80, 26, 53, and 57% yields, respectively.

Elongation of conjugation through ethyne bridge usually gives rise to a significant bathochromic shift of both **Table 2.** Pd-catalyzed Suzuki–Miyaura cross-coupling reactions of arylhalide with B2C2.^a



^{*a*} Reaction conditions: aryl halide = 67.6 μ mol (4 equiv to B2C2), B2C2 = 4.8 mg, Pd(OAc)₂ = 6 mol% to B2C2, P(^tBu)₃ = 3.5 mg, (P(^tBu)₃/Pd(OAc)₂ = 4), base = ⁱPr₂NH (6 equiv), solvent = DMSO, additive = dibutylhydroxytoluene (BHT, 1 mg),

temperature = 200 °C microwave, reaction time = 5 min. ^b Yield based on ¹H-NMR.



Figure 1. Excitation and emission spectra of (a) 1,2-bis(9-phenanthrenyl)ethyne (**2**), (b) 1,2-bis(1-pyrenyl)ethyne (**3**), and (c) 1,2-bis (9-anthryl)ethyne (**1**).

absorption and emission spectral envelopes. We measured fluorescence emission spectra of compounds 1-3. As the absorption spectra of these compounds have already been

Table 3. Fluorescence excitation and emission data of compounds 1-3.^{*a*}

Compound	λ_{max} (ex), nm	λ _{max} (em), nm	$\Phi_{ m f}$	Stoke shift, cm ⁻¹
1^{b}	462	494	0.60	1402
2 ^c	368	445	1.00	4702
3^d	433	442	0.81	470

^{*a*} Experimental conditions: solvent = CH_2Cl_2 , $T = 23 \pm 1$ °C.

 $^{b}\lambda_{ex} = 440 \text{ nm}, \lambda_{em} = 510 \text{ nm}.$

 $^{c} \lambda_{ex} = 360 \text{ nm}, \lambda_{em} = 470 \text{ nm}.$

 d $\lambda_{\text{ex}} = 400 \text{ nm}, \lambda_{\text{em}} = 460 \text{ nm}.$



Figure 2. Frontier molecular orbital (10 highest occupied and 10 lowest unoccupied) energy diagram of three diarylethynylene compounds calculated at the B3LYP/6-31g(d) level. Gradual destabilization of HOMO energy levels and concomittant stabilization of LUMO energy levels are guided by the dotted lines.

reported,^{17,19,20} we measured fluorescence excitation spectra to closely examine the origin of their fluorescence signatures. Figure 1 displays spectral features of three compounds and spectroscopic data are summarized in Table 3.

It is worth noting that both compounds 1 and 2 have significant Stoke shifts of 1402 and 4702 cm⁻¹, respectively, with broadened spectral features for emission spectra indicating that large degrees of structural relaxations are pertinent in the excited state. Compound 3, however, exhibited only 470 cm⁻¹ of Stoke shift with characteristic mirror image of excitation and emission spectra. $E_{0,0}$ values estimated by the intersection of excitation and emission spectra are 3.01, 2.84, and 2.61 eV for compounds 2, 3, and 1, respectively, exhibiting gradual decreasing of S1 state energies. Fluorescence quantum yields also decreased in the same order; 1.00, 0.81, and 0.61 for compounds 2, 3, and 1, respectively. Perhaps the energy gap law is the major background for the sharply decreasing fluorescence quantum yield upon decreasing $E_{0,0}$ values. Time-dependent density functional theory calculations performed in the gas phase indicate that the lowest energy absorptions of all three compounds are solely HOMO-to-LUMO transitions. The frontier orbital energy levels as well as the isosurfaces of HOMO and LUMO are illustrated in Figure 2. HOMO–LUMO gaps are gradually decreased by destabilization of HOMO and concomitant stabilization of LUMO levels for compounds **2**, **3**, and **1**, which are in accordance with experimentally determined $E_{0,0}$ values. This work clearly demonstrates an efficient electronic interaction between two polyaromatic units through ethyne bridge.

In conclusion, we have developed a new synthetic protocol in which Pd-catalyzed Suzuki–Miyaura cross-coupling reactions between aryl halide and B2C2 have been adapted for the synthesis of polyaromatic bisarylethynes in high yield. The three prepared compounds, **1–3**, show significant bathochromic shifts upon the elongation of conjugation through ethyne bridge.

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Supporting Information. Experimental and calculation details are available in the online version of this article.

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