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Synthesis and characterization of oxadisilole fused benzo[*b*]triphenylene

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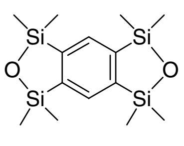
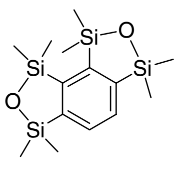
Abstract—Palladium-catalyzed [2+2+2] cyclotrimerization reactions between benzyne and oxadisilole fused oxabicyclic alkenes afforded the *exo*-adducts. Deoxygenation with $BF_3{\cdot}OMe_2$ yielded mono- and bis-oxadisilole fused benzo[*b*]triphenylene. The photophysical properties of the oxadisilole fused benzo[*b*]triphenylenes were characterized.

Benzyne is an important intermediate in organic synthesis.[1] It has been extensively used in the construction of natural and unnatural products.[2] Recently, we explored the benzyne generation chemistry from benzobisoxadisiloles (**1a** and **1b**) and benzotrisoxadisilole (**3**), and reported that they can serve as the synthetic equivalents of 1,4-benzdiyne (**2a**) and 1,3-benzdiyne (**2b**), respectively.[3] The chemistry was further extended to the synthesis and isolation of oxadisilole fused isobenzofurans (**4a** and **5a**) and isoindoles (**4b** and **5b**), and their applications in the preparation of functional acenes and benzoquinones.[4,5]

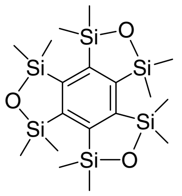
Transition-metal-mediated [2+2+2] cyclotrimerization reactions have been an active research area.[6] The pioneer work of Vollhardt in the 70s and 80s used cobalt as the metal catalyst. The use of benzyne as one of the π-2 components of the metal-mediated [2+2+2] cyclotrimerization, in particular under catalytic conditions, has drawn special attention in the past couple years. For example, Peña reported palladium-catalyzed cyclotrimerization of benzynes to yield triphenylenes.[7] Later, alkynes were also included as one of the reactive components by Peña and Yamamoto.[8] Alkenes[9] and most recently aryl halides[10] were also investigated as partners in [2+2+2] cyclotrimerization reactions. In 2004, sterically strain bicyclic alkenes was also first introduced as an active component in this versatile palladium-catalyzed [2+2+2] cyclotrimerization reactions by Cheng and co-workers.[11] In this Letter, we would like to report



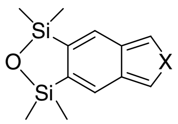
1a



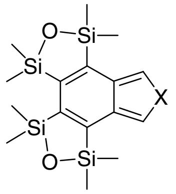
1b



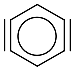
3



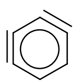
4a-b
a: X = O
b: X = N-BOC



5a-b



2a



2b

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our findings in the palladium-catalyzed [2+2+2] cyclotrimerization of oxadisilole fused bicyclic alkenes (**6a** and **6b**) with benzyne.

The bicyclic alkenes are the furan cycloadducts of benzynes generated from **1** and **3**, respectively.[4] After deoxygenation followed by aromatization, benzoxadisilole fused benzo[*b*]triphenylene (dibenz[*a*,*c*]anthracene) can be prepared. The photophysical properties of these previously unknown oxadisilole fused polycyclic aromatic compounds were characterized. Benzo[*b*]triphenylenes are potential useful materials for opto-electronics[12] and discotic liquid crystals.[13]

Using our phenyliodination-fluoride induced elimination protocol, benzoxadisilole fused bicyclic alkenes[4] **6a** and **6b** were prepared by trapping the benzynes generated from **1** and **3** with furan in 88% and 42% yield, respectively.[4] With $PdCl_2(PPh_3)_2$ as catalyst (5 mol %), mono-oxadisilole fused bicyclic alkene **6a** reacted smoothly with benzyne (generated from 2-(trimethylsilyl)phenyl triflate **7**) in CH_3CN at room temperature. The [2+2+2] cyclotrimerization product **8a** was isolated in 86% yield (Scheme 1). The assignment of the stereochemistry of **8a** as an *exo*-adduct was first based on the NMR arguments. It is well known that for norbornene derivatives, the coupling constant between the ring juncture *endo*-proton and the bridgehead proton is nearly zero.[11,14] The NMR spectrum ($CDCl_3$) of **8a** showed two bridgehead protons (H_a) as singlets at δ 5.40 ppm. The two protons on the norbornanephenanthracene ring junction (H_b) also appeared as singlets at δ 3.49 ppm. There is no coupling between H_a and H_b. Finally, the *exo*-stereochemistry of the [2+2+2] cycloadduct is confirmed by X-ray analysis (Fig. 1).[15]

Similarly, Pd-catalyzed [2+2+2] cyclotrimerization of the benzobisoxadisilole fused bicyclic alkene **6b** with benzyne afforded **8b** in 85% yield with high *exo*-stereoselectivity (singlets at 5.37 and 3.45 ppm for the bridgehead and ring juncture protons).

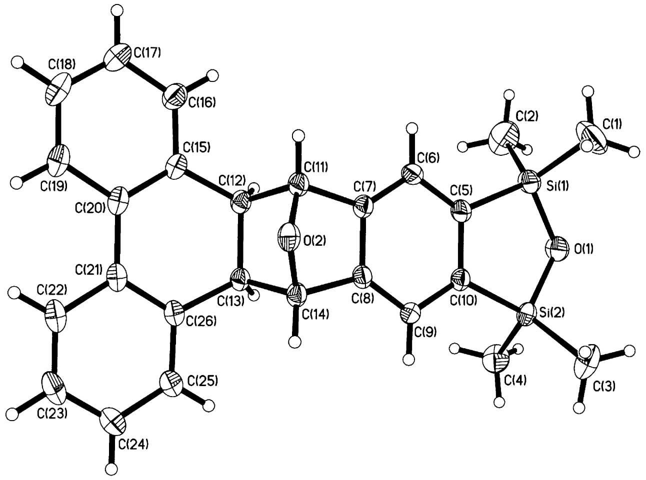
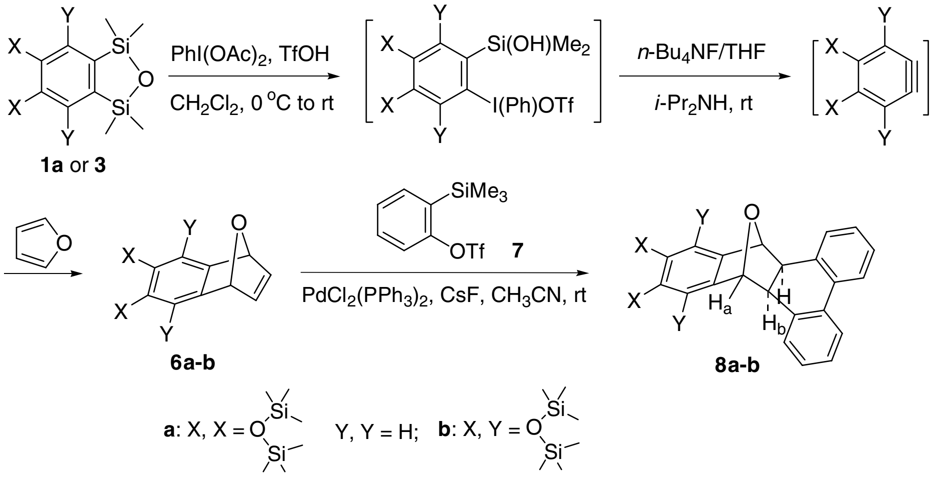


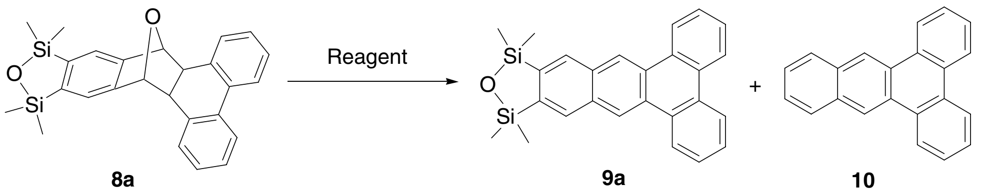
Figure 1. X-ray structure of **8a**.

Deoxyaromatization of the cyclotrimerization products with Lewis acid were investigated.[11] Upon treatment of **8a** with 1.5 equiv of $BF_3{\cdot}OMe_2$ for 1 h at rt, benzo[*b*]triphenylene **9a** was obtained in 32% yield with 56% recovery of the starting material **8a** (Scheme 2, entry 1). On extending the reaction time to 25 h, **9a** was isolated in 50% yield with 31% of the starting material **8a** recovered (entry 2). Further extending the reaction time did not improve the conversion. Although the reaction did not go to completion, **9a** can be readily isolated in pure form.[16] To our surprise, treatment of compound **8a** with 20 equiv of $BF_3{\cdot}OMe_2$, The parent benzo[*b*]triphenylene **10** was the only product formed in 58% yield (entry 3). With other Lewis acid such as $AlCl_3$ (entry 4), compound **10** was the only isolated product without **9a**. Even with 90% acetic acid (entry 5) at 100 °C, **10** could be obtained in 41% as the only isolated product. For some unknown reasons, the oxadisilole group was lost under these conditions. When purified **9a** was treated with 20 equiv of $BF_3{\cdot}OMe_2$ in CH_2Cl_2, it was found that **10** was formed under this condition, but not with 1.5 equiv of $BF_3{\cdot}OMe_2$.

A similar observation appeared for benzobisoxadisilole compound (**8b**). With 1.5 equiv of $BF_3{\cdot}OMe_2$ (Scheme 2, entry 6), bis-oxadisilole fused benzo[*b*]triphenylene

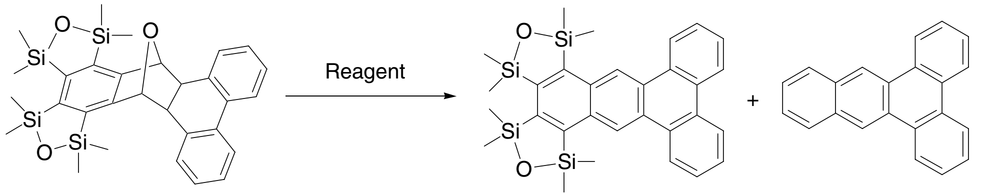


Scheme 1.



8a **9a** **10**

Entry				Recovery of 8a
1	$BF_3{\cdot}OMe_2$ (1.5 equiv), DCM, rt, 1 h	32%	–	56%
2	$BF_3{\cdot}OMe_2$ (1.5 equiv), DCM, rt, 25 hrs	50%	–	31%
3	$BF_3{\cdot}OMe_2$ (20 equiv), DCM, rt, 16 hrs	–	58%	–
4	$AlCl_3$, DCM, rt, 20 mins	–	25%	–
5	90% AcOH, 100 °C	–	41%	–



8b **9b** **10**

Entry				Recovery of 8b
6	$BF_3{\cdot}OMe_2$ (1.5 equiv), DCM, rt, 16 hrs	44%	–	25%
7	$BF_3{\cdot}OMe_2$ (20 equiv), DCM, rt, 16 hrs	–	53%	–

Scheme 2.

9b[17] was isolated in 44% yield with 25% of the starting material (**8b**) recovered. Using 20 equiv of $BF_3{\cdot}OMe_2$, the parent benzo[*b*]triphenylene **10** was the only product isolated in 53% yield (entry 7). Compounds **9a** and **9b** are readily soluble in common organic solvents such as $CHCl_3$ and CH_2Cl_2. These compounds can be purified by column chromatography on silica gel using a gradient of 2% EtOAc in petroleum ether (60–80 °C) as the eluant.

Due to high mobilities for hole transport, benzo[*b*]triphenylene derivatives are potential materials for organic electronics such as organic light-emitting diodes (OLED) and organic field effect transistors (OTFT).[18] The photophysical and redox properties of our newly synthesized mono- and bis-oxadisilole fused benzo[*b*]triphenylenes (**9a** and **9b**) were further characterized. The dates are summarized in Table 1.

Both oxadisilole fused benzo[*b*]triphenylenes exhibit bathochromic shifts of the strong β-band absorptions (i.e., Δ 9–14 nm)[19] and the long wavelength absorptions, which are characterized with sharp and fine structure (i.e., Δ 7–12 nm)[19] as compared to those of parent

Table 1. Summaries of physical measurements of benzo[*b*]triphenylene series

Compounds	$\lambda_{max}^{abs\ a}$ (nm) (ε_{max} (10^3 $M^{-1}cm^{-1}$))	$\lambda_{max}^{em\ a,b}$ (nm)	Φ_{FL}[a,c]	E_{ox}[d] (V)	T_m (T_{dec}[e]) (°C)
10	324 (0.74)	379	0.06	1.13 (ir, 2e)	206 (319)
9a	331 (1.01)	386	0.11	1.07 (ir, 1e)	317 (344)
9b	336 (1.11)	388	0.15	1.25 (ir, 1e)	269 (330)

[a] Measured in $CHCl_3$.

[b] Excited at the absorption maxima.

[c] Using 9,10-diphenylanthracene in cyclohexane ($\Phi_{360} = 0.90$) as a standard.

[d] E_{ox} Estimated by CV method in CH_3CN using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode with an agar salt bridge connecting to compounds solution and ferrocene was used as an external standard, $E_{1/2}$ (Fc/Fc^+) = 0.40 V versus SCE.

[e] Determined by thermal gravimetric analyzer with a heating rate of 10 °C/min under N_2.

benzo[*b*]triphenylene (**10**). Consistently, the oxadisilole fused benzo[*b*]triphenylenes (**9a** and **9b**) also exhibit a red shift of the emission (i.e., Δ 7–9 nm).[20] In general, the more the oxadisilole substitution, the longer are the absorption and emission wavelengths shifted. The more the oxadisiole substitution, the fluorescence quantum yields of these benzo[*b*]triphenylene derivatives was enhanced.

As silyl group is known to play the roles of σ-donating and π-withdrawing,[21] the position and the number of oxadisiole substitution therefore show profound effect on the redox properties of this benzo[*b*]triphenylene series as studied by cyclic voltammetry, which was carried out in a three-electrode cell set-up with 0.1 M of Bu_4NPF_6 as a supporting electrolyte in CH_3CN. All the potentials reported are referenced to Fc/Fc$^+$ standard and the results are tabulated in Table 1. Mono-oxadisiole fused benzo[*b*]triphenylene **9a** exhibits an irreversible one-electron oxidation corresponding to the formation of cation, with E_{pa} at 1.07 V, which is slightly lower than that of the parent benzo[*b*]triphenylene **10**. This suggests that oxadisiole substituted at the 6,7-position of benzo[*b*]triphenylene ring acting as a σ-electron donor stabilizes the formation of the cation. In contrast, the bis-5,6,7,8-oxadisiole substituted benzo[*b*]triphenylene **9b**, which exhibits a irreversible one-electron oxidation with $E_{1/2}$ at 1.25 V, did not show an enhanced stabilization of the cation as compared to that of parent benzo[*b*]triphenylene **10**. This indicates that the π-electron withdrawing role of oxadisiole group in such a substitution pattern becomes significant. These results suggest that the σ-donating or π-withdrawing role of oxadisiole group can easily be tuned by the number and the position of oxadisiole substitution on the aromatic ring.

Two new oxadisilole substituted benzo[*b*]triphenylenes are readily soluble in common organic solvents. The thermal stability of the benzo[*b*]triphenylene derivatives was also determined by TGA analyses.

In summary, two new mono- and bis-oxadisilole fused benzo[*b*]triphenylene **9a** and **9b** were synthesized via palladium-catalyzed [2+2+2] cyclotrimerization reaction followed by deoxyaromatization. These benzo[*b*]triphenylene derivatives were characterized. The σ-donating or π-withdrawing role of oxadisiole group is greatly affected by the number and the position of oxadisiole substitution on the aromatic ring. In general, as compared with the parent benzo[*b*]triphenylene, the quantum yields of these oxadisilole substituted derivatives were increased. Further study of the potential applications of these newly synthesized oxadisilole fused benzo[*b*]triphenylenes in optoelectronics is in progress.

Acknowledgments

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15. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 633049.
16. Compound **9a**: mp 316–318 °C; ^{1}H NMR (400 MHz) δ 0.49 (s, 12H), 7.65–7.70 (m, 4H), 8.34 (s, 2H), 8.59–8.61 (m, 2H), 8.78–8.80 (m, 2H), 9.12 (s, 2H); ^{13}C NMR (101 MHz) δ 1.3, 122.4, 123.5, 123.7, 127.6, 127.7, 129.0, 130.1, 130.2, 131.5, 132.3, 143.8; IR (KBr, cm^{-1}): 2954, 1249, 1091, 925; HRMS for $C_{26}H_{24}OSi_2$: $[M]^+$ calcd 408.1365, found 408.1353.
17. Compound **9b**: mp 268–270 °C; ^{1}H NMR (400 MHz) δ 0.54 (s, 12H), 0.75 (s, 12H), 7.68–7.74 (m, 4H), 8.62–8.68 (m, 4H), 9.12 (s, 2H); ^{13}C NMR (101 MHz) δ 2.3, 2.4, 122.9, 123.2, 123.7, 127.8, 127.9, 128.9, 129.9, 130.2, 133.4, 150.5, 140.9; IR (KBr, cm^{-1}): 2956, 1251, 944; HRMS for $C_{30}H_{34}O_2Si_4$: $[M]^+$ calcd 538.1635, found 538.1617.
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19. The difference between two β-band absorption cut off.
20. The difference between two absorption or emission maxima.
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