JOC Article

Oxadisilole-Fused Isobenzofurans. Synthesis and Characterization of Oxadisilole-Substituted Acenes

Ya-Li Chen, Chun-Kit Hau, Hao Wang, Hao He, Man-Shing Wong, and Albert W. M. Lee*

Department of Chemistry and Centre for Advanced Luminescence Materials,
Hong Kong Baptist University, Kowloon Tong, Hong Kong, China

alee@hkbu.edu.hk

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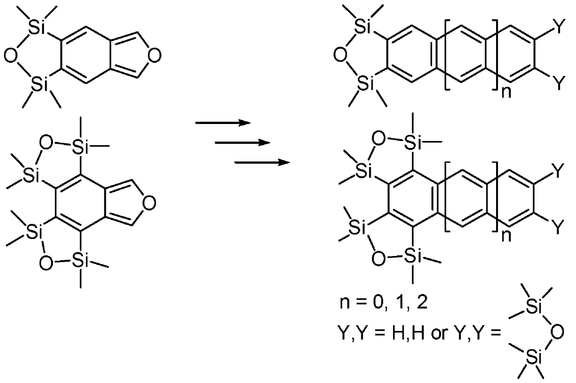
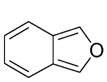


Mono- and bis-oxadisilole-fused isobenzofurans were first synthesized and isolated. A series of mono-, bis-, and tris-oxadisilole-substituted acenes were then synthesized by benzyne Diels−Alder reactions with the isobenzofurans. The photophysical, redox, and thermal properties of these new acenes were characterized.

Introduction

Isobenzofuran (IBF, benzo[*c*]furan, **1**) is a 10-electron system with four double bonds and two lone pair electrons. It is much more reactive than furan (a 6-electron system) in [4 + 2] cycloaddition, because after the reaction, a benzene structure is generated. IBF was first conclusively verified in 1964[1,2] and later isolated in the 1970s.[3] The parent IBF is only stable at low temperature, and electron-withdrawing substituents on the furanoid ring tend to stabilize the system. For example, 1-cyano-5,6-(methylenedioxy)benzo[*c*]furan is a stable crystalline solid, and its structure has been determined by crystallography.[4]

There are several known methods for generation of IBF.[5−9] Among them, the Warrener Diels−Alder/retro-Diels−Alder approach[3,9] with 3,6-di-2-pyridyl-1,2,4,5-tetrazine (**12**) is still one of the most reliable and efficient methods for IBF synthesis. In this paper, we report the first synthesis and isolation of mono- and bis-oxadisilole-fused isobenzofurans (**2** and **3**) with benzobisoxadisilole **4** and benzotrisoxadisilole **5** as the starting materials. Their applications in the synthesis of oxadisilole fused linear acenes are also described.



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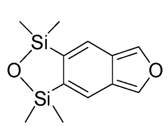

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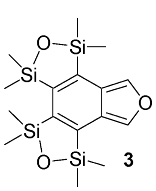

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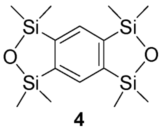

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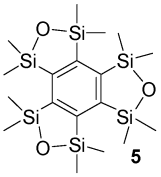

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Results and Discussion

The synthesis of mono- and bis-oxadisilole-fused isobenzofurans (**2** and **3**) is outlined in Scheme 1. Benzynes **8** and **9**

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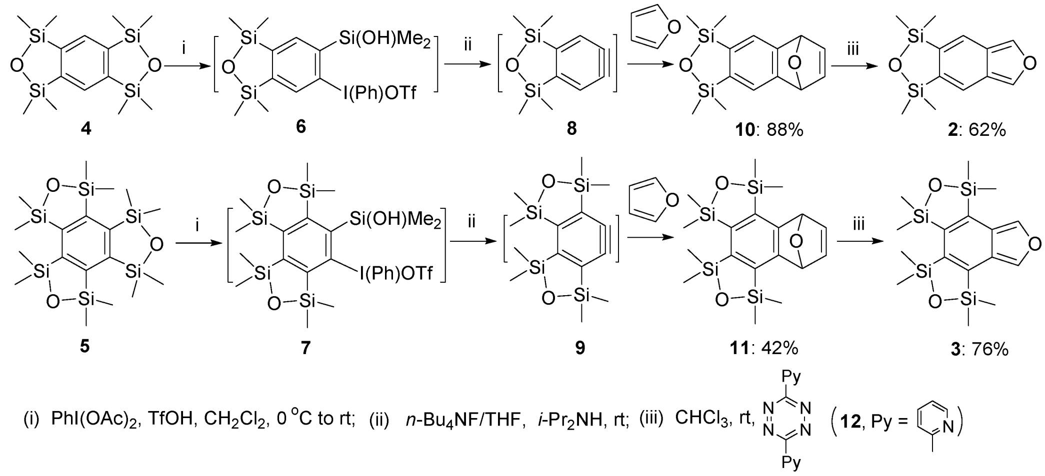
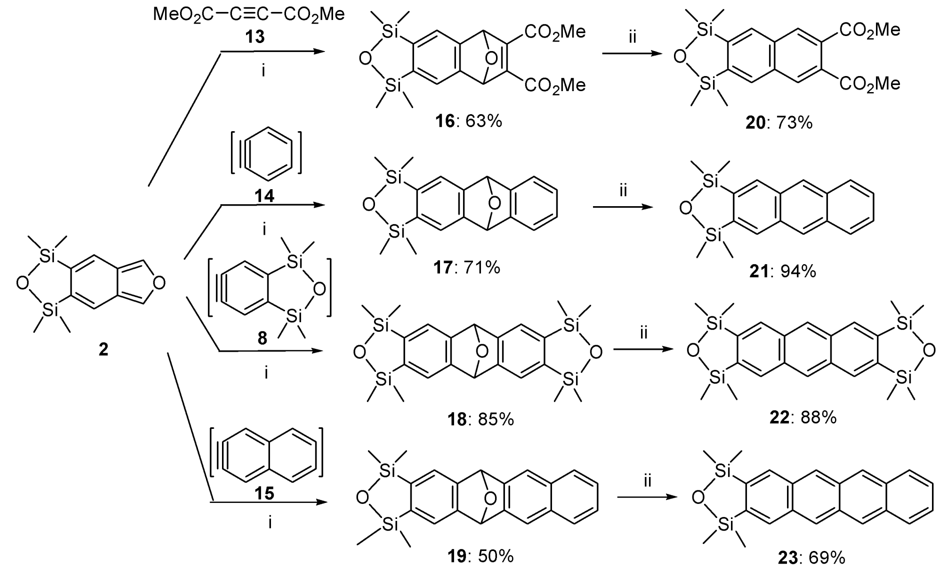
SCHEME 1



(i) PhI(OAc)$_2$, TfOH, CH$_2$Cl$_2$, 0 °C to rt; (ii) *n*-Bu$_4$NF/THF, *i*-Pr$_2$NH, rt; (iii) CHCl$_3$, rt,

SCHEME 2



(i) CHCl$_3$; (ii) LiAlH$_4$, TiCl$_4$, Et$_3$N, THF, reflux

were generated from benzobisoxadisilole **4** and benzotrisoxadisilole **5**, respectively, through our previously reported phenyliodination fluoride induced desilylation protocol.[10,11] Trapping benzynes **8** and **9** with furan afforded cycloadducts **10** and **11**. Cycloaddition reactions with tetrazine **12** at room temperature followed by spontaneous retro-cycloaddition and nitrogen extrusion under the Warrener protocol afforded the target molecules mono- and bis-oxadisilole-fused isobenzofurans **2** and **3** in good overall yields.

These previously unknown oxadisilole-fused isobenzofurans are stable white crystalline solids with sharp melting points. When stored under nitrogen and kept in the dark, these newly synthesized isobenzofurans were stable at room temperature within a week. As compared with other unstable isobenzofurans, this extra stability probably is due to the π-withdrawing property of the silyl groups. In general, probably due to steric reasons, the bis-oxadisilole-fused IBF **3** is more stable than mono-oxadisilole-fused IBF **2**. They can be purified by column chromatography on silica gel. However, for convenience, they are stored in dilute solutions of dichloromethane and used immediately after purification. The ^{1}H and ^{13}C NMR signals of **2** and **3** indicated the aromatic character of the isobenzofuran moieties. Attempts were made to prepare single crystals of **2** and **3** for X-ray analysis but failed.

[4 + 2] cycloaddition reactions of the mono- and bis-oxadisilole-fused isobenzofurans **2** and **3** with various dienophiles are summarized in Schemes 2 and 3. They reacted readily at room temperature with dimethyl acetylenedicarboxylate (DMAD, **13**),[12] parent benzyne (**14** generated from 1,2-dibromobenzene with *n*-BuLi), oxadisilole-fused benzyne (**8**), and 2,3-naphthyne (**15**).[11] The yields of the cycloaddition reactions are generally good. As compared with a similar set of reactions with furan,[10] the yields of these IBF reactions were lower. It is because in the furan-trapping experiments, excess (10-fold) amounts of furan were used. Previously, we also reported the dimerization of **8** when it reacted with furan. However, in the present set of reactions, no dimer of the trapping

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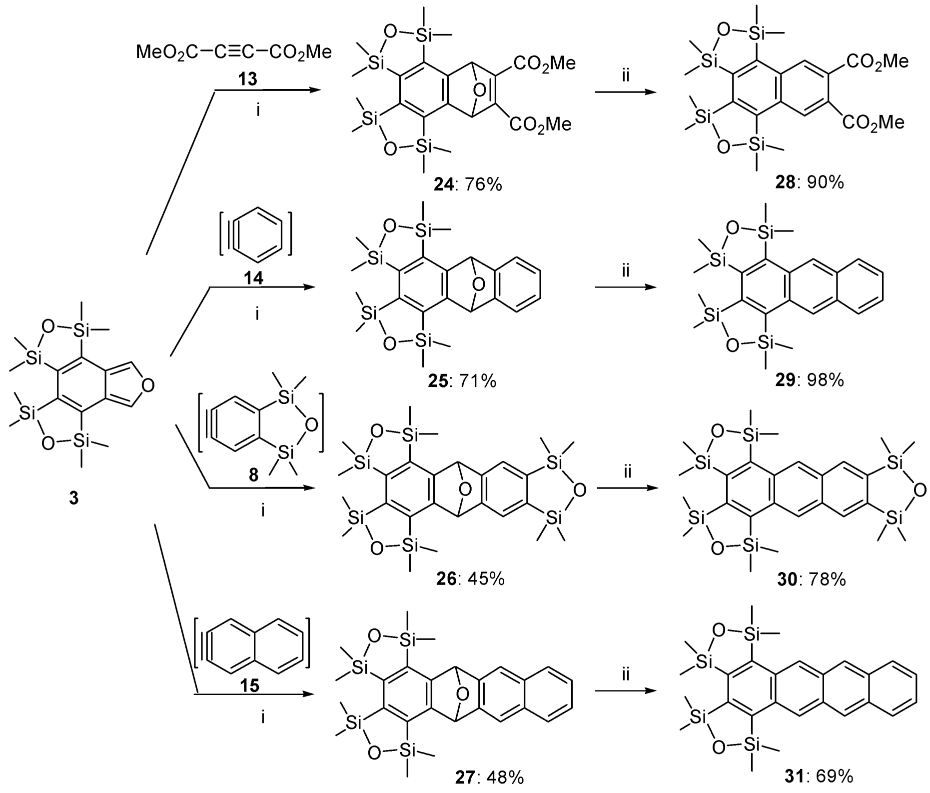
SCHEME 3



(i) $CHCl_3$; (ii) $LiAlH_4$, $TiCl_4$, Et_3N, THF, reflux

benzynes could be observed. Deoxygenation of the cycloadducts (**16**–**19** and **24**–**27**) with $TiCl_4/LiAlH_4/Et_3N$ afforded a series of mono-, bis-, and tris-oxadisilole-fused linear acenes (**20**–**23** and **28**–**31**) in reasonably good yields. To the best of our knowledge, this represents the first systematic approach to the preparation of these previously unknown oxadisilole linear fused acenes.[13]

Due to their high mobilities for hole transport, acene derivatives are useful materials for organic electronics such as organic light-emitting diodes (OLED) and organic field effect transistors (OTFT).[14,15] For example, Anthony has introduced a series of organic solvent soluble silylethynylated pentacene derivatives with interesting properties and applications in OLED.[16] On the other hand, the works of Nuckolls on acene motifs had led to the applications in thin film transistors and other organic electronics.[17] The photophysical and redox properties of our newly synthesized oxadisilole fused acenes were further characterized (Table 1).

TABLE 1. Summaries of Physical Measurements of Anthracene and Tetracene Series

compd	λ_{max}^{abs} ^{a}/nm ($\epsilon_{max}/10^3$ M^{-1} cm^{-1})	λ_{max}^{em} ^{a,b}/nm	Φ_{FL} ^{a,c}	E_{ox} ^{d}/V	T_m (T_{dec} ^{e})/°C
anthracene	359 (5.92)	396	0.17	0.94 (ir, 2e)	213 (221)
21	370 (4.49)	412	0.15	0.91 (ir, 2e)	152 (223)
29	372 (7.60)	413	0.17	0.92 (r, 2e)	234 (248)
22	381 (6.38)	426	0.38	0.86 (ir, 2e)	349 (313)
30	382 (8.03)	427	0.33	0.84 (r, 2e)	268 (269)
tetracene	475 (5.20)	478	0.08	0.50 (r, 1e), 1.08 (ir, 2e)	>300 (314)
23	489 (5.43)	494	0.07	0.49 (r, 1e), 1.08 (ir, 2e)	233 (277)
31	486 (7.17)	492	0.09	0.54 (r, 1e), 1.06 (ir, 2e)	259 (273)

[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 in anthracene series, using fluorescein in 0.1 N NaOH ($\Phi_{436} = 0.92$) as a standard in tetracene series. [d] E_{ox} estimated by CV method in CH_2Cl_2 using a platinum disk electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode with an agar salt bridge connecting to compound solution, and ferrocene was used as an external standard, $E_{1/2}$ (Fc/Fc^+) = 0.47 V vs SCE. [e] Determined by thermal gravimetric analyzer with a heating rate of 10 °C/min under N_2.

All of the oxadisiole-substituted acenes exhibit bathochromic shifts of the strong β-band absorption (i.e., Δ 10–25 nm for anthracene series and Δ 11–22 nm for tetracene series)[18] and the long wavelength absorptions, which are characterized with sharp and fine structure (i.e., Δ 11–23 nm for anthracene series

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(18) The difference between two β-band absorption cutoff.

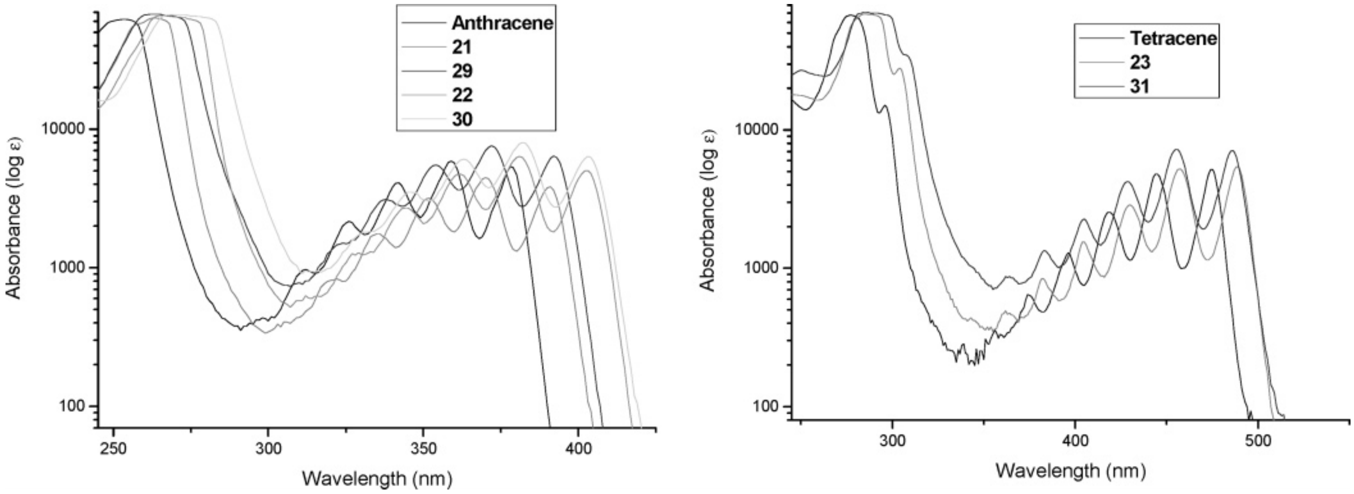

FIGURE 1. Absorption spectra of anthracene and tetracene series measured in $CHCl_3$.

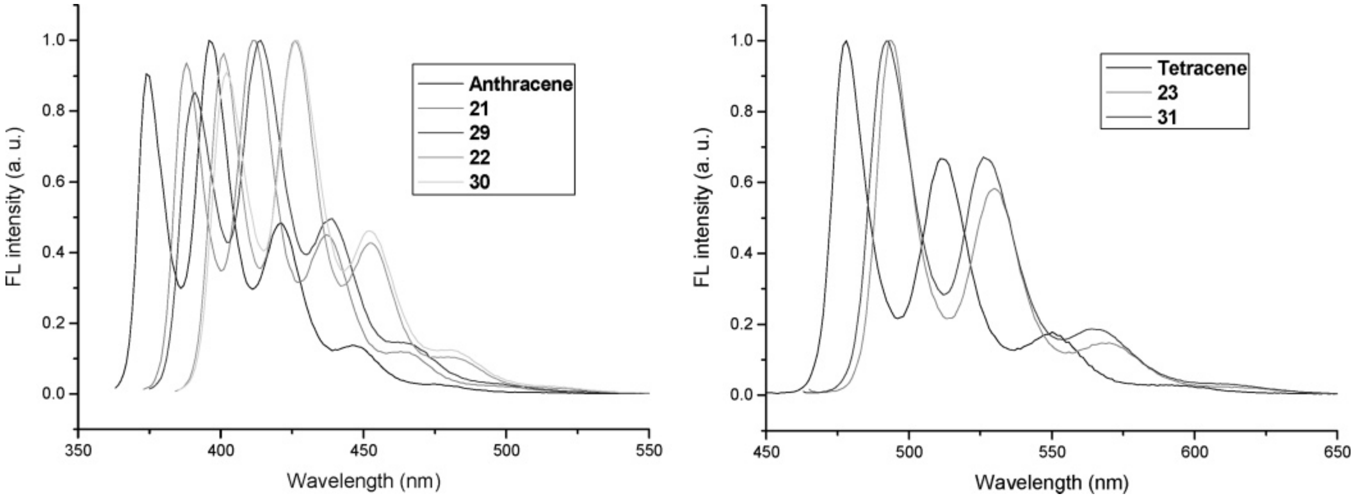

FIGURE 2. Emission spectra of anthracene and tetracene series measured in $CHCl_3$.

and Δ 11−14 nm for tetracene series)[19] as compared to those of the parent acenes. In general, the more the oxadisiole substitution, the longer are the absorption wavelengths shifted (Figure 1). Consistently, the oxadisiole-substituted acenes also exhibit a red shift of the emission (i.e., Δ 16−31 nm for anthracene series and Δ 14−16 nm for tetracene series)[19] relative to that of the corresponding acene. In addition to the absorption, the emission wavelengths of these acene derivatives increase with the extent of conjugation (Figure 2). In general, the fluorescence quantum yields of these acene derivatives are not affected by mono-2,3- or bis-1,2,3,4-oxadisiole substitution (**21** and **29**); however, bis-2,3,6,7-oxadisiole substitution, i.e., **22**, and multiple oxadisiole substitution, i.e., **30**, would greatly enhance the fluorescence quantum yields of acene derivatives.

As the silyl group is known to play the roles of σ-donating and π-withdrawing,[13] the position and the number of oxadisiole substitution therefore show profound effects on the redox properties of this acene series as studied by cyclic voltammetry, which was carried out in a three-electrode cell setup with 0.1 M of Bu_4NPF_6 as a supporting electrolyte in CH_2Cl_2. All of the potentials reported are referenced to Fc/Fc^+ standard, and the results are tabulated in Table 1. 2,3-Oxadisiole-substituted anthracene, **21**, exhibits an irreversible two-electron oxidation, corresponding to the formation of dication, with E_{pa} at 0.91 V, which is slightly lower than that of parent anthracene. This suggests that oxadisiole substituted at the 2,3-position of the anthracene ring acting as a σ-electron donor stabilizes the formation of the dication. Furthermore, second oxadisiole-substitution to the corresponding conjugated positions (para-type) as in the case of bis-2,3,6,7-oxadisiole-substituted anthracene, **22**, leads to further reduction of the first oxidation potential ($E_{pa} = 0.86$ V). In contrast to the para-disubstitution, ortho-disubstitution as in the case of bis-1,2,3,4-oxadisiole-substituted anthracene **29**, which exhibits a reversible two-electron oxidation with $E_{1/2}$ at 0.92 V, do not show an enhanced stabilization of the dication as compared to that of mono-substitution. This indicates that the π-electron-withdrawing role of the oxadisiole group in such a substitution pattern becomes significant. With an increase in the acene unit, the first oxidation of 2,3-oxadisiole-substituted tetracene becomes a reversible one-electron oxidation process and occurs at a lower potential; on the other hand, the stabilizing effect of the oxadisiole group reduces indicating the weak σ-donating nature of the oxadisiole group. Consistently, the bis-1,2,3,4-oxadisiole substitution (ortho-disubstitution) (i.e., **31**) dominantly enforced by the π-electron-

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[19] The difference between two absorption or emission maxima.

withdrawing contribution leads to a higher first oxidation potential indicating that the cation is destabilized as compared to the parent tetracene. 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 acene ring.

In addition to enhancing the solubility, the oxadisiole substitution improves the thermal stability of the anthracene derivatives as determined by TGA analyses.

In summary, two previously unknown oxadisilole-fused isobenzofurans were synthesized and isolated. They were used as the building blocks for the preparation of oxadisilole fused linear acenes. A series of mono-, bis-, and tris-oxadisilole-fused anthracenes and tetracenes were synthesized and 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 acene ring. In general, as compared with the parent anthracene, the thermal stability of these oxadisilole substituted derivatives were increased. The extension of this protocol to the synthesis of other linear and angular acenes is in progress.

Experimental Section

Mono-oxadisilole-Fused Isobenzofuran 2. 3,6-Di-2-pyridyl-1,2,4,5-tetrazine (**12**, 283 mg, 1.20 mmol) was added to a stirred solution of **10** (274 mg, 1.00 mmol in 10 mL of $CHCl_3$) at room temperature under N_2. After compound **10** disappeared (monitored by TLC), solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 5% EtOAc in petroleum ether (60−80 °C) as eluent to afford compound **2** (154 mg, 0.62 mmol) in 62% yield: mp 120−122 °C; ^1H NMR (400 MHz) δ 0.37 (s, 12H), 7.65 (s, 2H), 8.04 (s, 2H); ^{13}C NMR (101 MHz) δ 1.2, 122.5, 124.2, 135.2, 140.4; IR (KBr, cm^{-1}) 2961, 2925, 1250, 1058, 937; HRMS for $C_{12}H_{16}O_2Si_2$ $[M + H]^+$ calcd 249.0767, found 249.0770.

Bis-oxadisilole-Fused Isobenzofuran 3. 3,6-Di-2-pyridyl-1,2,4,5-tetrazine (**12**, 283 mg, 1.20 mmol) was added to a stirred solution of **11** (404 mg, 1.00 mmol in 10 mL of $CHCl_3$) at room temperature under N_2. After the compound **11** disappeared (monitored by TLC), solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 5% EtOAc in petroleum ether (60−80 °C) as eluent to afford compound **3** (287 mg, 0.76 mmol) in 76% yield: mp 131−133 °C; ^1H NMR (400 MHz) δ 0.43 (s, 12H), 0.44 (s, 12H), 8.03 (s, 2H); ^{13}C NMR (101 MHz) δ 0.8, 2.3, 123.1, 135.8, 142.7, 147.7; IR (KBr, cm^{-1}) 2958, 1257, 1046, 924; HRMS for $C_{16}H_{26}O_3Si_4$ $[M + H]^+$ calcd 379.1037, found 379.1022.

Cycloadduct 16 from Diels−Alder Reaction of IBF 2 with DMAD 13. A freshly prepared solution of IBF **2** (from 274 mg, 1.00 mmol of **10** in 10 mL of $CHCl_3$) was reacted with DMAD **13** (0.15 mL, 1.20 mmol) at room temperature. After 2 h, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 5−10% EtOAc in petroleum ether (60−80 °C) as eluent to afford compound **16** (246 mg, 0.63 mmol) in 63% yield: mp 112−114 °C; ^1H NMR (400 MHz) δ 0.33 (s, 6H), 0.35 (s, 6H), 3.82 (s, 6H), 5.96 (s, 2H), 7.60 (s, 2H); ^{13}C NMR (101 MHz) δ 0.9, 1.0, 52.4, 84.7, 123.4, 147.1, 147.2, 150.8, 162.8; IR (KBr, cm^{-1}) 2955, 1738, 1705, 1438, 1294, 1252, 1214, 1100, 938; HRMS for $C_{18}H_{22}O_6Si_2$ $[M + Na]^+$ calcd 413.0852, found 413.0856.

Cycloadduct 17 from Diels−Alder Reaction of IBF 2 with Benzyne 14. *n*-BuLi (1.50 mL of a 1.60 M solution in dry hexane, 2.40 mmol) was added to a mixture of dibromobenzene (236 mg, 1.00 mmol) and IBF **2** (124 mg, 0.50 mmol) in dry toluene (8 mL) at −78 °C over 4 h. The mixture was allowed to reach room temperature during 15 h and then was poured into 20 mL of water. The resulting mixture was extracted with CH_2Cl_2. The organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 2−5% EtOAc in petroleum ether (60−80 °C) as the eluent to afford product **17** (117 mg, 0.36 mmol) in 71% yield: mp 138−140 °C; ^1H NMR (400 MHz) δ 0.29 (s, 6H), 0.33 (s, 6H), 6.05 (s, 2H), 7.03−7.05 (m, 2H), 7.35−7.37 (m, 2H), 7.50 (s, 2H); ^{13}C NMR (101 MHz) δ 0.9, 1.1, 82.5, 120.5, 122.4, 126.0, 146.8, 147.9, 149.1; IR (KBr, cm^{-1}) 2954, 1248, 1096, 924; HRMS for $C_{18}H_{20}O_2Si_2$ $[M + H]^+$ calcd 325.1080, found 325.1086.

Cycloadduct 18 from Diels−Alder Reaction of IBF 2 with Oxadisilole-Fused Benzyne 8. A solution of IBF **2** (prepared from 658 mg, 2.40 mmol of **10** in 10 mL of $CHCl_3$) was added to a CH_2Cl_2 solution of oxadilole-fused benzyne **8**[10] prepared from benzobisoxadisilole **4** (338 mg, 1.00 mmol) at room temperature under N_2. The crude product was purified by column chromatography on silica gel using a gradient of 2−5% EtOAc in petroleum ether (60−80 °C) as eluent to afford compound **18** (386 mg, 0.85 mmol) in 85% yield: mp 356−358 °C; ^1H NMR (400 MHz) δ 0.30 (s, 12H), 0.33 (s, 12H), 6.03 (s, 2H), 7.52 (s, 4H); ^{13}C NMR (101 MHz) δ 0.9, 1.1, 82.4, 122.6, 146.9, 148.8; IR (KBr, cm^{-1}) 2957, 1253, 1093, 935; HRMS for $C_{22}H_{30}O_3Si_4$ $[M + Na]^+$ calcd 477.1169, found 477.1159.

Cycloadduct 19 from Diels−Alder Reaction of IBF 2 with 2,3-Naphthyne 15. A solution of IBF **2** (prepared from 658 mg, 2.40 mmol of **10** in 10 mL of $CHCl_3$) was added to a CH_2Cl_2 solution of 2,3-naphthyne **15** prepared from naphthoxadisilole[10] (258 mg, 1.00 mmol) at room temperature under N_2. The crude product was purified by column chromatography on silica gel using 2−5% EtOAc in petroleum ether (60−80 °C) as eluent to afford adduct **19** (187 mg, 0.50 mmol) in 50% yield: mp 192−194 °C; ^1H NMR (400 MHz) δ 0.25 (s, 6H), 0.33 (s, 6H), 6.18 (s, 2H), 7.41−7.43 (m, 2H), 7.53 (s, 2H), 7.71−7.74 (m, 4H); ^{13}C NMR (101 MHz) δ 0.9, 1.0, 82.2, 118.9, 122.4, 126.2, 128.1, 132.3, 143.7, 147.2, 148.2; IR (KBr, cm^{-1}) 2955, 1253, 1097, 924; HRMS for $C_{22}H_{22}O_2Si_2$ $[M + Na]^+$ calcd 397.1056, found 397.1231.

Diels−Alder Reactions of IBF 3. The reaction conditions of cycloaddition of IBF **3** with DMAD **13**, benzynes **14** and **8**, and 2,3-naphthyne **15** were similar to those for IBF **2**.

Cycloadduct 24: 76% yield; mp 168−169 °C; ^1H NMR (400 MHz) δ 0.38 (s, 6H), 0.42 (s, 12H), 0.47 (s, 6H), 3.82 (s, 6H), 5.94 (s, 2H); ^{13}C NMR (101 MHz) δ 1.2, 1.3, 2.3, 2.5, 52.4, 84.7, 141.6, 149.3, 150.3, 151.1 162.7; IR (KBr, cm^{-1}) 2957, 1740, 1718, 1438, 1255, 1213, 1104, 951; HRMS for $C_{22}H_{32}O_7Si_4$ $[M + Na]^+$ calcd 543.1122, found 543.1144.

Cycloadduct 25: 71% yield; mp 175−177 °C; ^1H NMR (400 MHz) δ 0.35 (s, 6H), 0.38 (s, 6H), 0.39 (s, 6H), 0.54 (s, 6H), 6.02 (s, 2H), 7.02−7.05 (m, 2H), 7.29−7.31 (m, 2H); ^{13}C NMR (101 MHz) δ 1.3, 1.5, 2.3, 2.4, 82.6, 120.5, 126.1, 140.3, 147.8, 149.9, 151.1; IR (KBr, cm^{-1}) 2957, 1254, 1104, 931; HRMS for $C_{22}H_{30}O_3Si_4$ $[M + Na]^+$ calcd 477.1169, found 477.1166.

Cycloadduct 26: 45% yield; mp 251−253 °C; ^1H NMR (400 MHz) δ 0.29 (s, 6H), 0.34 (s, 6H), 0.37 (s, 6H), 0.39 (s, 6H), 0.40 (s, 6H), 0.55 (s, 6H), 6.00 (s, 2H), 7.45 (s, 2H); ^{13}C NMR (101 MHz) δ 0.8, 1.1, 1.3, 1.4, 2.3, 2.4, 82.5, 122.4, 140.5, 147.1, 148.8, 149.9, 150.9; IR (KBr, cm^{-1}): 2957, 1254, 1098, 937; HRMS for $C_{26}H_{40}O_4Si_6$ $[M + Na]^+$ calcd 607.1440, found 607.1417.

Cycloadduct 27: 48% yield; mp 298−300 °C; ^1H NMR (400 MHz) δ 0.31 (s, 6H), 0.39 (s, 6H), 0.45 (s, 6H), 0.57 (s, 6H), 6.15 (s, 2H), 7.42−7.45 (m, 2H), 7.64 (s, 2H), 7.72−7.74 (m, 2H); ^{13}C NMR (101 MHz) δ 1.4, 1.6, 2.27, 2.33, 82.3, 118.9, 126.3, 128.2, 132.2, 140.4, 143.5, 150.2, 150.4; IR (KBr, cm^{-1}) 2957, 1254, 943; HRMS for $C_{26}H_{32}O_3Si_4$ $[M + 1]^+$ calcd 505.1506, found 505.1499.

Preparation of Acenes 20, 21, 22, 23, 28, 29, 30, and 31 by Deoxygenation of 16, 17, 18, 19, 24, 25, 26, and 27. Typical Procedure: Compound 20. $TiCl_4$ (3.1 mL, 28 mmol) was carefully added to a suspension of $LiAlH_4$ (380 mg, 10 mmol) in 10 mL of anhydrous THF at 0 °C, followed by Et_3N (5.0 mL, 36 mmol) under

N_2. The mixture was stirred for 30 min at 0 °C and then allowed to warm to room temperature. A solution of **16** (312 mg, 0.80 mmol) in 10 mL of anhydrous THF was added. The mixture was refluxed for 12 h and then was poured into crushed ice (10 g) containing 10 mL of 1 N HCl. The resulting mixture was extracted with CH_2Cl_2. The organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 5−10% EtOAc in petroleum ether (60−80 °C) as the eluent to afford product **20** (218 mg, 0.58 mmol) in 73% yield: mp 175−177 °C; ^{1}H NMR (400 MHz) δ 0.44 (s, 12H), 3.96 (s, 6H), 8.12 (s, 2H), 8.27 (s, 2H); ^{13}C NMR (101 MHz) δ 1.1, 52.7, 128.8, 130.5, 131.7, 133.4, 147.6, 168.1; IR (KBr, cm^{-1}) 2954, 1737, 1722, 1438, 1283, 1255, 1092, 931; HRMS for $C_{18}H_{22}O_5Si_2$ [M + Na]$^+$ calcd 397.0903, found 397.0902.

Acene 21. Starting with **17** (259 mg, 0.80 mmol), acene **21** (232 mg, 0.75 mmol) was isolated as a white solid in 94% yield: mp 151−153 °C; ^{1}H NMR (400 MHz) δ 0.48 (s, 12H), 7.47−7.49 (m, 2H), 8.02−8.04 (m, 2H), 8.26 (s, 2H), 8.45 (s, 2H); ^{13}C NMR (101 MHz) δ 1.3, 125.5, 126.6, 128.3, 131.7, 131.8, 132.1, 142.5; IR (KBr, cm^{-1}) 2956, 1252, 1074, 930; HRMS for $C_{18}H_{20}OSi_2$ [M + H]$^+$ calcd 309.1130, found 309.1135.

Acene 22. Starting with **18** (363 mg, 0.80 mmol), acene **22** (308 mg, 0.70 mmol) was isolated as a white solid in 88% yield: mp 348−350 °C; ^{1}H NMR (400 MHz) δ 0.47 (s, 24H), 8.24 (s, 4H), 8.45 (s, 2H); ^{13}C NMR (101 MHz) δ 1.3, 127.1, 131.9, 132.2, 142.8; IR (KBr, cm^{-1}): 2953, 1255, 1070, 930; HRMS for $C_{22}H_{30}O_2Si_4$ [M + Na]$^+$ calcd 461.1221, found 461.1211.

Acene 23. Starting with **19** (299 mg, 0.80 mmol), acene **23** (198 mg, 0.55 mmol) was isolated as a yellow solid in 69% yield: mp 232−234 °C; ^{1}H NMR (400 MHz) δ 0.48 (s, 12H), 7.40−7.42 (m, 2H), 7.99−8.02 (m, 2H), 8.25 (s, 2H), 8.69 (s, 4H); ^{13}C NMR (101 MHz) δ 1.3, 125.2, 126.5, 126.8, 128.3, 130.6, 131.4, 131.6, 132.0, 142.1; IR (KBr, cm^{-1}) 2953, 1248, 1066, 937; HRMS for $C_{22}H_{22}OSi_2$ [M + Na]$^+$ calcd 381.1106, found 381.1112.

Compound 28. Starting with **24** (416 mg, 0.80 mmol), compound **28** (363 mg, 0.72 mmol) was isolated as a white solid in 90% yield: mp 214−216 °C; ^{1}H NMR (400 MHz) δ 0.48 (s, 12H), 0.58 (s, 12H), 3.98 (s, 6H), 8.22 (s, 2H); ^{13}C NMR (101 MHz) δ 1.9, 2.3, 52.8, 129.0, 130.5, 135.1, 151.4, 153.5, 168.0; IR (KBr, cm^{-1}) 2955, 1727, 1434, 1277, 1258, 1226, 1071, 936; HRMS for $C_{22}H_{32}O_6Si_4$ [M + H]$^+$ calcd 505.1354, found 505.1366.

Acene 29. Starting with **25** (363 mg, 0.80 mmol), acene **29** (343 mg, 0.78 mmol) was isolated as a white solid in 98% yield: mp 233−235 °C; ^{1}H NMR (400 MHz) δ 0.52 (s, 12H), 0.67 (s, 12H), 7.53−7.55 (m, 2H), 8.04−8.07 (m, 2H), 8.40 (s, 2H); ^{13}C NMR (101 MHz) δ 2.0, 2.4, 125.9, 127.3, 128.3, 132.0, 132.5, 149.7, 151.3; IR (KBr, cm^{-1}) 2954, 1254, 952; HRMS for $C_{22}H_{30}O_2Si_4$ [M + 1]$^+$ calcd 439.1401, found 439.1385.

Acene 30. Starting with **26** (467 mg, 0.80 mmol), acene **30** (354 mg, 0.62 mmol) was isolated as a white solid in 78% yield: mp 268−270 °C; ^{1}H NMR (400 MHz) δ 0.48 (s, 12H), 0.51 (s, 12H), 0.66 (s, 12H), 8.27 (s, 2H), 8.40 (s, 2H); ^{13}C NMR (101 MHz) δ 1.3, 2.0, 2.4, 127.8, 131.8, 132.0, 133.0, 143.4, 149.8, 151.5; IR (KBr, cm^{-1}) 2956, 1253, 931; HRMS for $C_{26}H_{40}O_3Si_6$ [M]$^+$ calcd 568.1593, found 568.1571.

Acene 31. Starting with **27** (403 mg, 0.80 mmol), acene **31** (269 mg, 0.55 mmol) was isolated as yellow solid in 69% yield: mp 258−260 °C; ^{1}H NMR (400 MHz) δ 0.51 (s, 12H), 0.69 (s, 12H), 7.44−7.46 (m, 2H), 8.03−8.05 (m, 2H), 8.62 (s, 2H), 8.72 (s, 2H); ^{13}C NMR (68 MHz) δ 2.1, 2.5, 125.4, 126.5, 127.5, 128.1, 130.3, 131.7, 132.1, 149.5, 151.6; IR (KBr, cm^{-1}) 2957, 1254, 942; HRMS for $C_{26}H_{32}O_2Si_4$ [M]$^+$ calcd 488.1479, found 488.1495.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all new compounds and absorption and emission spectra of oxadisilole-substituted acenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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