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Oxadisilole fused pentacenequinones and heptacenequinones

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Abstract

Stable, organic solvent soluble bis- and tetrakis-oxadisilole fused pentacenequinones (**5a**–**b**) and heptacenequinones (**11a**–**b**) were synthesized. Double Diels–Alder and fourfold aldol-condensation approaches were used. Absorption, emission and fluorescence quantum yield of the previously unknown acenequinones **5a** and **11a** were characterized. The role of the oxadisilole substituent on the photophysical properties was addressed.

Keywords: Oxadisilole fused pentacenequinone; Oxadisilole fused heptacenequinone; Double Diels–Alder reaction; Fourfold aldol-condensation

Linear acenes have been widely studied as potential materials for organic electronics[1,2] such as organic field effect transistors (FETs)[3,4] and organic light-emitting diodes (OLEDs).[5] As compared with the inorganic counter parts, organic molecules offer several advantages such as flexibility and lower cost of fabrication. It is believed that these acenes and related organic materials with high hole transport charge-carrier mobility may one day replace the inorganic based electronic and lighting devices. However, many of the parent higher acenes are rather unstable and have very poor solubility in common organic solvents that complicate the fabrication process. In contrary, the corresponding higher acenequinones are much more stable.

Acenequinones have many interesting photophysical properties that may find practical applications. For example, recently, it was reported that the alkoxy substituted linear *para*-acenequinones are emissive dyes with large dichroic ratios in liquid crystal mixtures.[6] *para*-Acenequinones are also common precursors for many acenes derivatives with interesting photophysical properties. For example, a series of stable trialkylsilylethynyl substituted acenes derivatives with good solubility and photophysical properties have been prepared from the corresponding *para*-quinones.[7–11] To follow our efforts on the preparation and characterization of oxadisilole fused linear[12] and angular[13] acenes, we would like to report our findings in the synthesis of oxadisilole fused penta- and heptacenequinones.

The preparation of the pentacenequinone series is outlined in Scheme 1. A double Diels–Alder approach[14] with mono- and bis-oxadisilole fused isobenzofurans (IBF) as the building blocks was adopted. Following our reported procedures,[12] the IBFs (**3a** and **3b**) were generated in situ by reacting oxabicyclic compounds **1a** and **1b** with 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (**2**). Trapping the IBFs with 0.5 equiv of *p*-benzoquinone afforded double Diels–Alder adducts **4a** and **4b**[15] as single diastereomer in both cases. X-ray structure of adduct **4a** confirmed the *anti*-stereochemical arrangement of the oxygen bridges[16] (Fig. 1).

Double dehydration of adducts **4a** and **4b** with acetic acid at 100 °C afforded bis- and tetrakis-oxadisilole fused pentacenequinones **5a** and **5b**[15] in good yields. The

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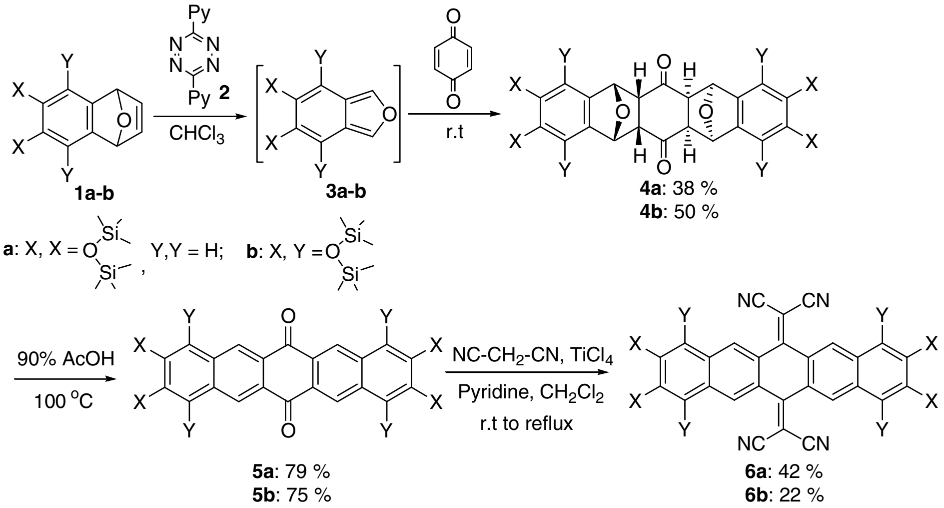


Scheme 1. The preparation of pentacenequinones **5a** and **5b**.

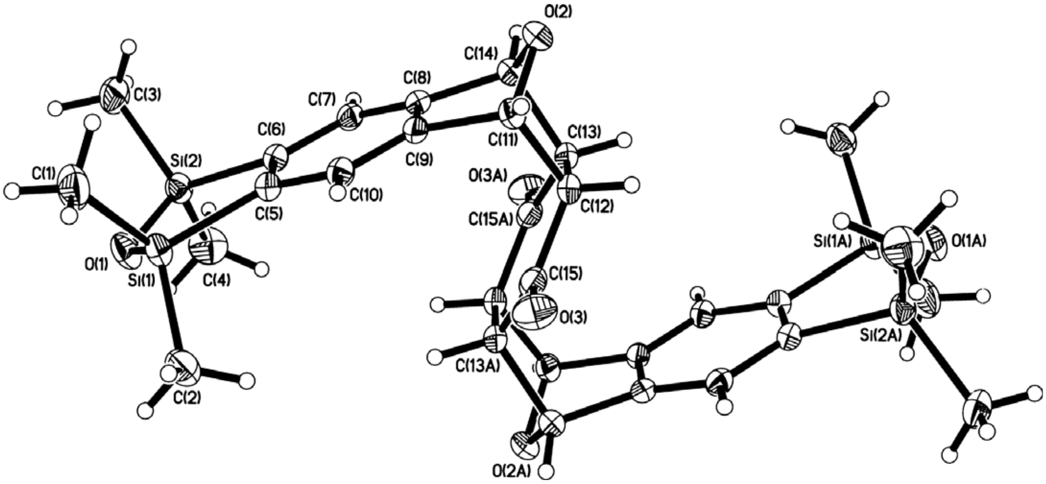
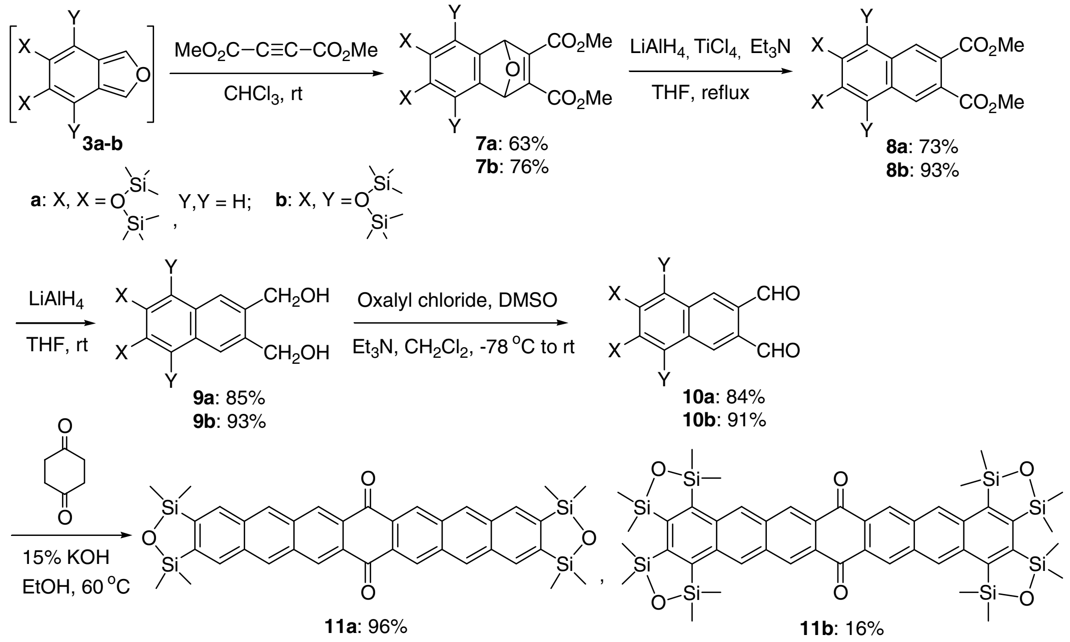


Fig. 1. X-ray structure of **4a**.

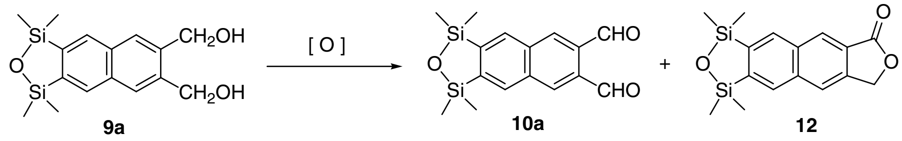
tetracyano compounds **6a** and **6b**[15] were also prepared by reacting with malononitrile in the presence of $TiCl_4$[17–19] (Scheme 1).

As outlined in Scheme 2, the heptacenequinones series was prepared using a fourfold aldol-condensation approach with 1,4-cyclohexanedione.[11,20,21] The corresponding dialdehydes (**10a** and **10b**) could be prepared from diesters **8a** and **8b**[12] through a reduction–oxidation cycle (Scheme 2). The reduction of **8a**–**b** with $LiAlH_4$ went smoothly. However, the re-oxidation to dialdehyde was troublesome (Scheme 3). Various amounts of lactone **12** that is the half-oxidized product were formed when pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), or $[Ag(C_5H_5N)_2]MnO_4$[22] were used as the oxidants. Eventually, Swern oxidation solved the problem to yield **10a** and **10b** in good yields. Subsequent fourfold aldol-condensation in alcoholic KOH with 1,4-cyclohexanedione afforded bis- and tetrakis-oxadisilole fused heptacenequinones **11a** and **11b**.[23]

The bis- and tetrakis-oxadisilole fused pentacenequinones and heptacenequinones are readily soluble in common organic solvents such as dichloromethane, chloroform, and tetrahydrofuran. The bis-oxadisilole heptacenequinone **11a** exhibits bathochromic shifts of the strong β-band absorptions (Δ 30 nm)[24] and the long wavelength absorptions, which are characterized with sharp and fine structures (Δ 53 nm)[25] as compared to those of the bis-oxadisilole pentacenequinone **5a**. It also exhibits a red-shift of the emission (Δ 81 nm)[25] relative to that of **5a**. In general, the absorption and emission wavelengths of these acenequinone derivatives increase with the extent of conjugation. The fluorescence quantum yield of pentacenequinone **5a** is unexpectedly



Scheme 2. The preparation of heptacenequinones **11a** and **11b**.



	10a	12
PCC	2%	68%
PDC	29%	38%
$[Ag(C_5H_5N)_2]MnO_4$	30%	36%
Oxalyl chloride, DMSO Et_3N, CH_2Cl_2, -78 °C to rt	84%	0%

Scheme 3. The oxidation of dialcohol **9a**.

Table 1
Comparison of physical measurements of acenequinones **5a** and **11a**

Compounds	λ_{max}^{abs} [a]/nm ($\varepsilon_{max}/10^3\ M^{-1}\ cm^{-1}$)	λ_{max}^{em} [a,b]/nm	Φ_{FL} [a,c]	T_m/°C	T_{dec} [d]/°C
5a	417 (1.23)	437	0.01	>360	387
11a	470 (3.50)	518	0.16	>360	445

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

low as compared with that of heptacenequinone **11a**. Their thermal stabilities were also determined by TGA analyses (Table 1).

In summary, a series of previously unknown bis- and tetrakis-oxadisilole fused pentacenequinones and heptacenequinones were synthesized by double Diels–Alder and fourfold aldol-condensation approaches. The study of the further transformation of these acenequinones, in particular the heptacenequinones, to other acene derivatives is in progress.

Acknowledgments

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15. Compound **4a**: mp 225–227 °C; ^{1}H NMR (400 MHz) δ 0.32 (s, 12H), 0.36 (s, 12H), 2.33–2.34 (m, 4H), 5.49–5.50 (m, 4H), 7.38 (s, 4H), 8.97 (s, 4H); ^{13}C NMR (101 MHz) δ 1.0, 1.1, 51.7, 82.5, 123.2, 143.3, 148.7, 205.6; IR (KBr, cm^{-1}): 2959, 1704, 1686, 1250, 1106, 927; HRMS for $C_{30}H_{36}O_6Si_4$: $[M+H]^+$ calcd 605.1667; found, 605.1671. Compound **4b**: mp 280–282 °C; ^{1}H NMR (400 MHz) δ 0.41 (s, 12H), 0.43 (s, 12H), 0.46 (s, 12H), 0.50 (s, 12H), 2.92 (s, 4H), 5.74 (s, 4H); ^{13}C NMR (101 MHz) δ 1.2, 1.4, 2.3, 2.4, 54.6, 82.4, 140.0, 146.1, 152.3, 205.5; IR (KBr, cm^{-1}): 2958, 1710, 1254, 946; HRMS for $C_{38}H_{56}O_8Si_8$: $[M+Na]^+$ calcd 887.2027; found, 887.1985. Compound **5a**: mp >360 °C; ^{1}H NMR (400 MHz) δ 0.48 (s, 24 H), 8.33 (s, 4H), 8.97 (s, 4H); ^{13}C NMR (101 MHz) δ 1.1, 130.2, 131.0, 133.1, 135.1, 148.8, 182.9; IR (KBr, cm^{-1}): 2924, 1676, 1265, 1252, 935; HRMS for $C_{30}H_{32}O_4Si_4$: $[M + H]^+$ calcd 569.1455; found, 569.1449. Compound **5b**: mp >360 °C; ^{1}H NMR (400 MHz) δ 0.52 (s, 24H), 0.68 (s, 24H), 8.96 (s, 4H); ^{13}C NMR (101 MHz) δ 2.0, 2.3, 129.9, 130.8, 136.9, 153.1, 154.9, 182.6; IR (KBr, cm^{-1}): 2958, 1678, 1257, 945; HRMS for $C_{38}H_{52}O_6Si_8$: $[M+H]^+$ calcd 829.1996; found, 829.1957. Compound **6a**: mp >360 °C; ^{1}H NMR (400 MHz) δ 0.46 (s, 24H), 8.24 (s, 4H), 8.75 (s, 4H); ^{13}C NMR (101 MHz) δ 1.0, 81.5, 113.7, 126.7, 129.4, 132.2, 133.3, 150.3, 161.7; IR (KBr, cm^{-1}): 2957, 2227, 1255, 1094, 941; HRMS for $C_{36}H_{32}N_4O_2Si_4$: $[M+H]^+$ calcd 665.1680; found, 665.1676. Compound **6b**: mp >360 °C; ^{1}H NMR (400 MHz) δ 0.47 (s, 12H), 0.52 (s, 12H), 0.63 (s, 12H), 0.76 (s, 12H), 8.63 (s, 4H); ^{13}C NMR (101 MHz) δ 2.3, 2.6, 82.1, 113.6, 127.2, 129.2, 135.5, 152.3, 156.1, 161.6; IR (KBr, cm^{-1}): 2956, 2923, 2228, 1256, 953; HRMS for $C_{44}H_{52}N_4O_4Si_8$: $[M+H]^+$ calcd 925.2215; found, 925.2215.
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23. Compound **11a**: mp >360 °C; ^{1}H NMR (400 MHz) δ 0.49 (s, 24H), 8.33 (s, 4H), 8.76 (s, 4H), 9.20 (s, 4H); ^{13}C NMR (101 MHz) δ 1.2, 129.9, 130.4, 131.7, 132.1, 132.2, 133.6, 145.6, 182.8; IR (KBr, cm^{-1}): 2956, 1675, 1298, 1253, 1227, 1076, 932; HRMS for $C_{38}H_{36}O_4Si_4$: $[M+H]^+$ calcd 669.1768; found, 669.1766. Compound **11b**: mp >360 °C; ^{1}H NMR (400 MHz) δ 0.53 (s, 24H), 0.71 (s, 24H), 8.73 (s, 4H), 9.27 (s, 4H); ^{13}C NMR (101 MHz) δ 2.0, 2.3, 130.1, 130.7, 131.6, 132.3, 134.9, 151.9, 152.6, 182.9; IR (KBr, cm^{-1}): 2957, 2923, 1680, 1254, 939; HRMS for $C_{46}H_{56}O_6Si_8$: $[M+Na]^+$ calcd 951.2128; found, 951.2155.
24. The difference between two β-band absorption cutoffs.
25. The difference between two absorption or emission maxima.