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Synthesis and Characterization of Novel Oligoazulenes with Mixed Ethynyl and Butadiynyl Bridges

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Dedicated to Professor Siegfried Hünig on the occasion of his 85th birthday

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The new oligoazulenes **10**–**14** with mixed ethynyl and butadiynyl bridges were synthesized by oxidative Eglinton coupling from the readily accessible ethynylazulenes **3**, **4**, **7**, **9** and **15** as well as by Pd/Cu-catalyzed cross-coupling reactions with the appropriate iodoazulenes **5**, **6** and **8**.

Introduction

The design and synthesis of conjugated oligomers or polymers have been a significant subject of many recent studies because of their numerous optical, electrochemical and electrical properties.[1–12] These compounds can serve as models for analogous bulk polymers and they can also be used for the constructions of nanoarchitectures such as molecular wires in molecular-scale electronic devices.[13,14] In particular, the construction of polyethynylated as well as donor- and/or acceptor-substituted benzenoid and heteroaromatic compounds have received much attention in the last decades.[15–21] In this respect, we recently reported the synthesis of mono- and polyethynylazulenes[22] and studied their synthetic utility as building blocks for the construction of novel cyclic conjugated π-electron systems[23] as well as conjugated molecular scaffolds with ethynylazulene or butadiynylazulene units **1a**–**e** and **2a**–**e**, respectively.[24,25] The pronounced polarizability of the azulene system[26] lets assume that oligoazulenes **1** and **2** could exhibit interesting electronic properties. In continuation of these studies, we report here on the syntheses of new oligoazulenes with both ethynyl and butadiynyl bridges by Pd/Cu-catalyzed as well as oxidative coupling reactions.

Results and Discussion

Synthesis of 3-Iodoazulenyl-Terminated Oligomers

At first our attention focused on the iodonation of oligoazulenes **1** and **2**[24,25] in order to develop a synthesis of 3-iodoazulenyl-terminated oligomers as building blocks for the construction of novel oligoazulenes with ethynylazulene or butadiynylazulene units by Pd/Cu-catalyzed cross coupling reactions[27–29] with the appropriate ethynylazulenes. Unfortunately, the straightforward iodonation of **1** and **2** with 1 or 2 equiv. of *N*-iodosuccinimide[22] was unsuccessful.

Contrary to this, the conventional Eglinton coupling[30,31] of the appropriate ethynyl(iodo)azulenes has proved to be an effective methodology for the synthesis of monoiodo and diiodo derivatives of butadiynyl-bridged oligoazulenes **2** as outlined in Scheme 1.

Thus, oxidative Eglinton coupling of 6-*tert*-butyl-1-ethynyl-3-iodoazulene (**3**)[24] with $Cu(OAc)_2$ in a boiling pyridine/methanol/diethyl ether mixture furnished 1,4-bis(6-*tert*-butyl-3-iodoazulen-1-yl)-1,3-butadiyne (**5**) as brown crystals in good yield (84%). On the other hand, oxidative coupling of 6-*tert*-butyl-1,3-diethynylazulene (**4**)[22,24] in the presence of **3** as end-capping reagent led to the formation of 6-*tert*-butyl-1,3-bis[(6-*tert*-butyl-3-iodoazulen-1-yl)butadiynyl]azulene (**6**) in 22% yield. In addition to the trimer **6**, also the dimer **5** could be isolated in 24% yield together with a mixture of probable higher oligomers. The inherent insolubility of the latter did not allow a chromatographic separation of pure samples.

Similar to **5**, also 1-(6-*tert*-butyl-3-iodoazulen-1-yl)-4-(6-*tert*-butylazulen-1-yl)-1,3-butadiyne (**8**) could be prepared in 40% yield by oxidative coupling of a mixture of **3** and 6-

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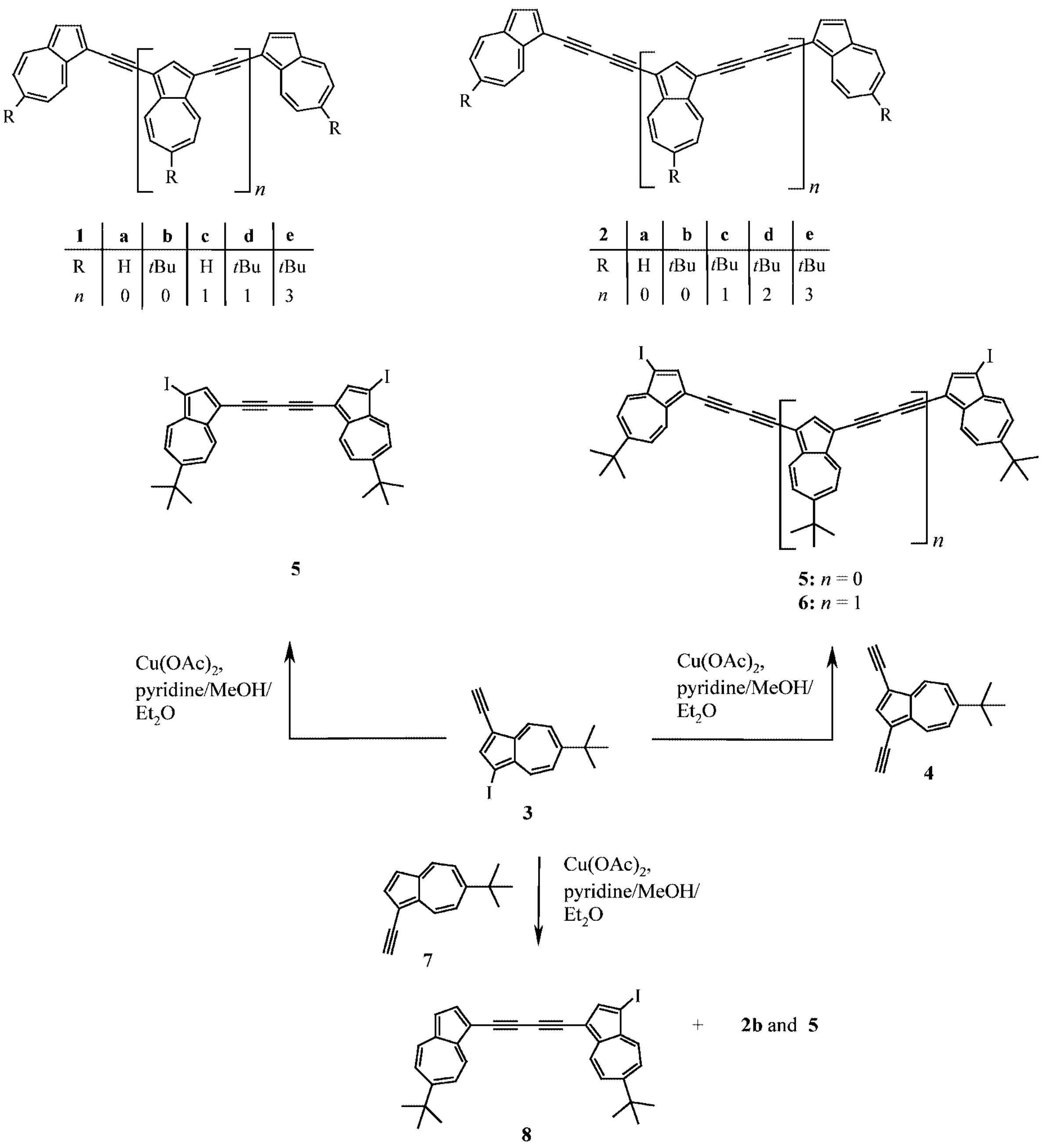


1	a	b	c	d	e
R	H	*t*Bu	H	*t*Bu	*t*Bu
n	0	0	1	1	3

2	a	b	c	d	e
R	H	*t*Bu	*t*Bu	*t*Bu	*t*Bu
n	0	0	1	2	3

Scheme 1.

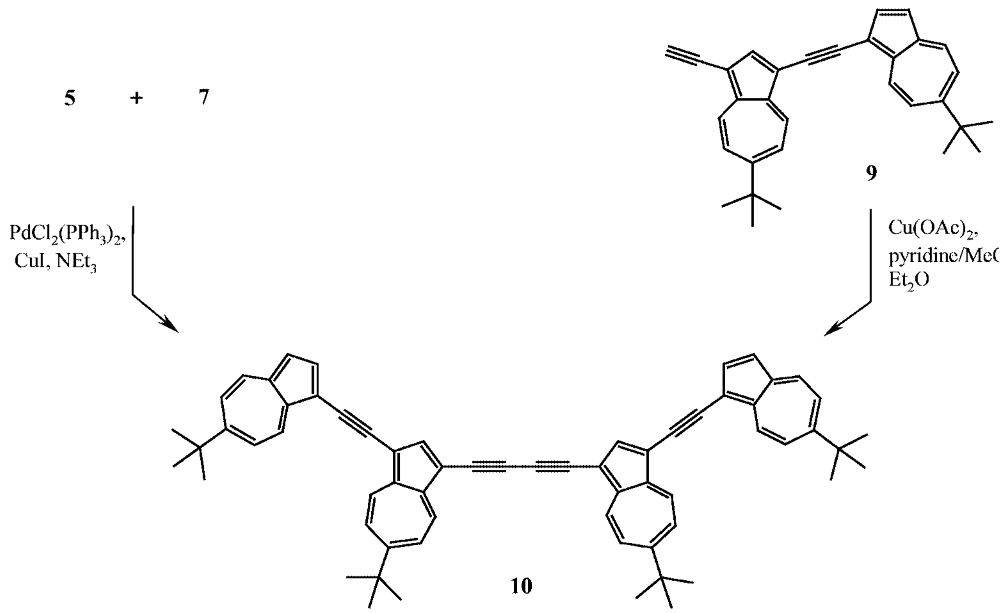
tert-butyl-1-ethynylazulene (**7**).[22,24] As a result of the homocoupling of **3** as well as **7**, also the dimers **5** (27%) and **2b** (24%) could be isolated from the reaction mixture.

Synthesis of Oligoazulenes 10–14 with Ethynyl and Butadiynyl Bridges

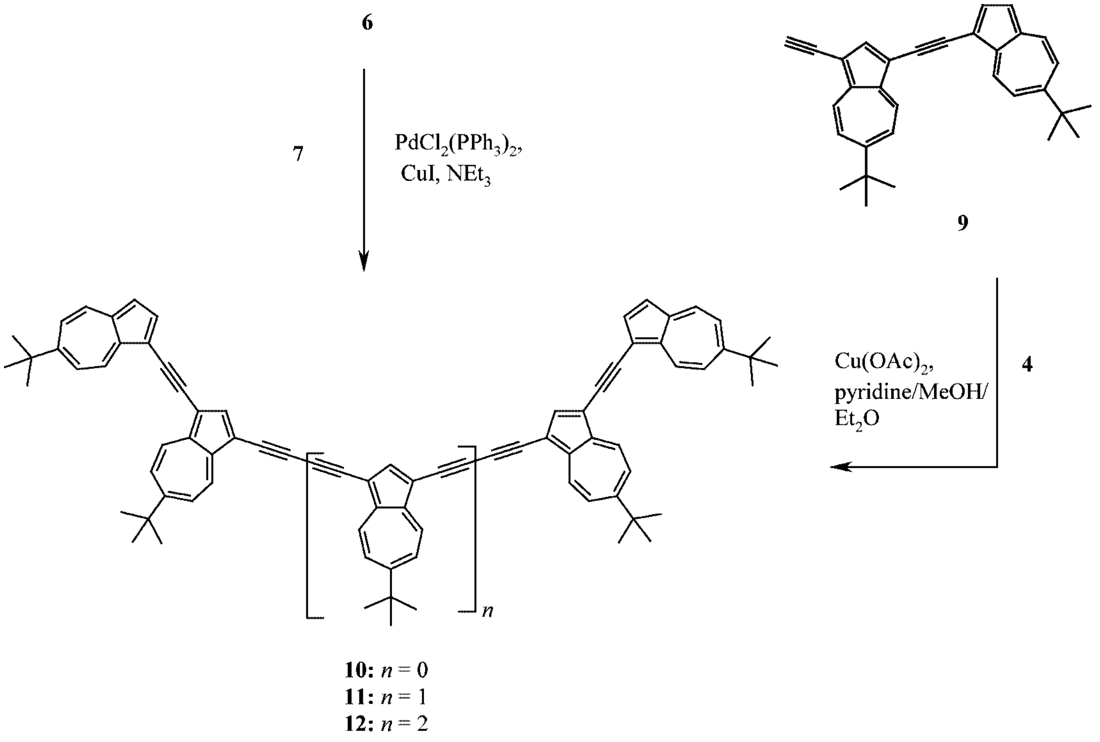
The utility of the new iodoazulene derivatives **5**, **6** and **8** as building blocks for the synthesis of further oligoazulenes was proved by Sonogashira coupling reaction. Thus, coupling of **5** with 2 equiv. of 6-*tert*-butyl-1-ethynylazulene (**7**) resulted in the formation of the tetramer **10** with 47% yield as green crystals. The same compound could be obtained by Eglinton coupling of 1-(6-*tert*-butyl-3-ethynylazulen-1-yl)-2-(6-*tert*-butylazulene-1-yl)ethyne (**9**)[24] using Cu(OAc)$_2$ in a boiling pyridine/methanol/diethyl ether mixture, which afforded **10** in 62% yield (Scheme 2).

Likewise, also the pentamer **11** with outer ethynyl and inner butadiynyl bridges can be synthesized (Scheme 3).

The Pd/Cu-catalyzed cross-coupling reaction of the trimer **6** with 2 equiv. of **7** afforded **11** as deep green crystals in 37% yield. The latter was alternatively obtained in 17% yield by oxidative coupling of a mixture of **4** and **9** using the common copper(II)-mediated coupling conditions [Cu(OAc)$_2$, pyridine/methanol/diethyl ether]. In addition to



Scheme 2.

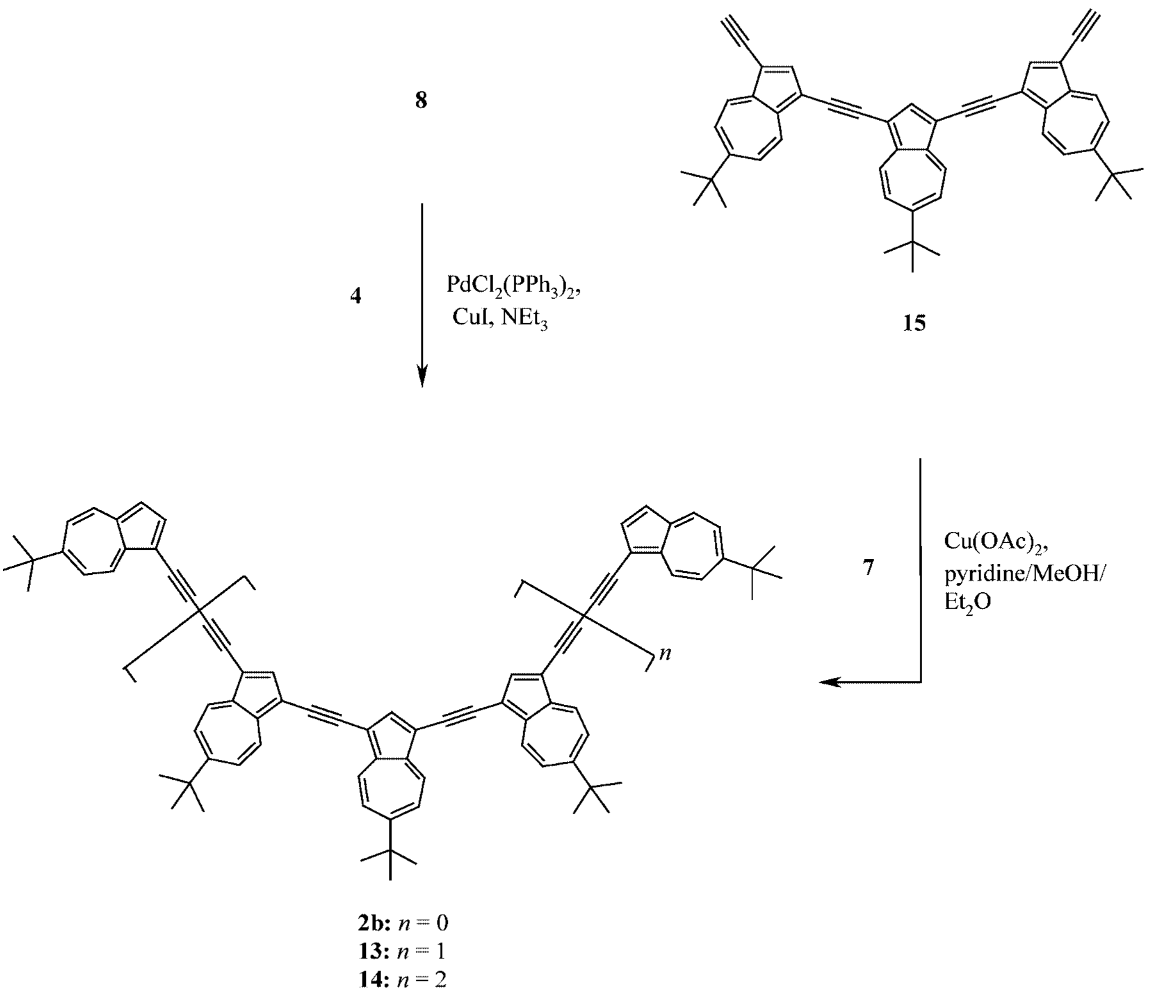


Scheme 3.

11, also the hexamer **12** as well as the tetramer **10** could be isolated as black and green crystals in 4% and 20% yields, respectively.

On the other hand, the pentamer **13** with outer butadiynyl and inner ethynyl bridges could be obtained by Pd/Cu-catalyzed cross-coupling reaction of **4** with 2 equiv. of **8** in 33% yield as black crystals. Compound **13** resulted also in 20% yield from the oxidative coupling of 6-*tert*-butyl-1,3-bis-{[(6-*tert*-butyl-3-ethynyl)azulen-1-yl]ethynyl}azulene (**15**)[24] in the presence of **7** as end-capping reagent. In addition, 3% of the octamer **14** and 24% of the dimer **2b** could be isolated (Scheme 4).

The structure of the novel oligoazulenes **10**–**14** was confirmed by IR, NMR, MS data as well as elemental analyses. The ^{1}H NMR spectra of the tetramer **10** exhibit a singlet at $\delta = 8.12$ ppm characteristic of the 2-H protons of the two



Scheme 4.

middle azulene rings. Those of pentamers **11**, **13** as well as hexamer **12** show two singlets at δ = 8.08–8.14 ppm, characteristic of the 2-H and 2′-H protons of the three and the four middle azulene rings, respectively, in a ratio of 1:2 (as in **11**, **13**) and in a ratio of 1:1 (as in **12**). The spectrum of octamer **14** shows three singlets at δ = 8.13, 8.15 and 8.20 ppm characteristic of the 2′′-H, 2′-H, and 2-H protons, respectively, of the six middle azulene rings in a ratio of 1:1:1.

Electronic Spectra of the Oligomers 10–14

The UV/Vis spectra of the new oligomers **10**–**14** are shown in Figure 1 and reveal some interesting conclusions:

(1) The spectra of the new oligoazulenes **10**–**14** surprisingly show only a small hypsochromic shift of the longest wavelength absorption maximum from 615 nm for the tetramer **10** to 610 nm for the octamer **14**, presumably due to a reduced conjugation. In contrast, the spectra of the ethynyl-bridged azulenes **1a**–**e** exhibit significant bathochromic shifts of the longest wavelength absorption maxima with increasing number of ethynyl units.

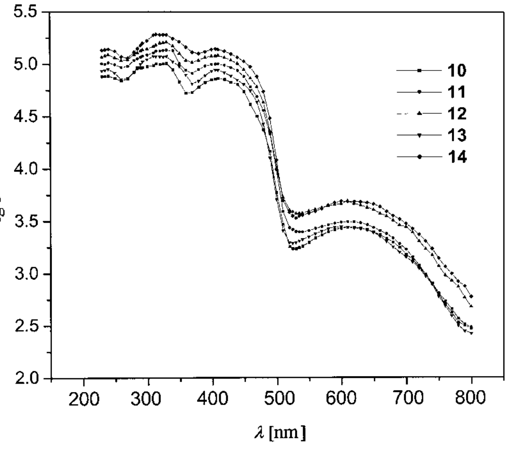


Figure 1.UV/Vis spectra of compounds **10**–**14** in dichloromethane.

(2) Replacement of the inner or the outer ethynyl bridges in the ethynyl-bridged pentamer **1e** by butadiynyl bridges is also accompanied by a hypsochromic shift of the longest wavelength absorption maximum (λ_{max}) from 625 nm (for

compound **1e**), to 612 nm (for compound **11**), 599 nm (for compound **13**) and 593 nm (for compound **2e**[25]).

(3) Interestingly, a replacement of the inner ethynyl bridges by butadiynyl bridges leads to a weaker hypsochromic shift of the longest wavelength absorption maximum (λ_{max}) than the replacement of the outer ones.

(4) Furthermore, the extinction coefficients of the pentamers **11** and **13** were found to be larger than that of the ethynyl-bridged pentamer **1e**.

Conclusions

We prepared 3-iodoazulenyl-terminated oligoazulenes, which are potentially new building blocks for the synthesis of novel oligoazulenes, with both ethynyl and butadiynyl bridges by Pd/Cu-catalyzed cross-coupling reaction with the corresponding ethynylazulenes. The novel oligoazulenes could also be obtained by Eglinton coupling of the appropriate ethynylazulenes. In most cases, the Pd/Cu-catalyzed cross-coupling methodology is superior to the oxidative Eglinton coupling since it offers better yields. However, the Eglinton coupling methodology allowed us to isolate higher oligomers, although in low yield.

Experimental Section

General: All melting points are uncorrected. IR spectra were measured with Beckman IR 5A and Perkin–Elmer 125 spectrometers. NMR spectra were recorded with a Bruker NMR spectrometer WM 300 in $CDCl_3$ with tetramethylsilane as internal standard. UV/Vis spectra were recorded with a Beckman UV-5240 spectrometer. Mass spectra (MS) were obtained with a Varian 311A instrument or a Bruker-Frantzen-Esquire-LC. Elemental analyses: Perkin–Elmer CHN 240 B. Column chromatography: Basic alumina [activity B II–III (Brockmann), ICN Biomedicals].

General Procedure for the Oxidative Coupling of Ethynylazulenes: A solution of the appropriate ethynylazulenes **3** or **9** (4 mmol) or a mixture (3:1) of (**3** and **4**), (**3** and **7**), (**9** and **4**) or (**7** and **15**) (4 mmol) in pyridine (10 mL) was added slowly over a period of 30 min to a boiling solution of copper(II) acetate [1.8 mg (10 mmol)] in a pyridine/methanol/diethyl ether mixture (50 mL, 1:1:4). The reaction mixture was heated under reflux for 2 h. The mixture was cooled to 0 °C and poured carefully into 2 N HCl (100 mL). Dichloromethane (50 mL) was added to the resulting suspension. The layers were separated and the aqueous solution was extracted with CH_2Cl_2 (4×50 mL). The combined organic layers were washed with water, dried with Na_2SO_4 and filtered. The solvent was removed in vacuo and the remaining residue was purified by column chromatography on alumina (B II–III) with CH_2Cl_2/*n*-hexane (1:4) for compounds **5**, **10**. The mixture (**5**, **6**) was separated by column chromatography on alumina (B II–III) with CH_2Cl_2/*n*-hexane (1:4). The mixtures (**2b**, **5**, **8**), (**10**, **11**, **12**) and (**2b**, **13**, **14**) were separated by column chromatography on alumina (B II–III) with CH_2Cl_2/*n*-hexane (1:7 → 1:4) for compounds **2b**, **5**, **8** and 1:4 → 1:2 for compounds **10**, **11**, **12** as well as **2b**, **13**, **14**.

1,4-Bis(6-*tert*-butyl-3-iodoazulen-1-yl)-1,3-butadiyne (5): **3** afforded **5** as brown crystals (2.10 g, 84%), m.p. > 260 °C. FT-IR (KBr): $\tilde{\nu}$ = 2946, 2856 (C–H), 2123 ($C{\equiv}C$), 1579, 1421, 1293, 847 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.47 [s, 18 H, $C(CH_3)_3$], 7.52–7.59 (m, 4 H, 5-, 7-H), 7.99 (s, 2 H, 2-H), 8.17 (d, $^{3}J_{H,H}$ = 10.6 Hz, 2 H, 4-H), 8.53 (d, $^{3}J_{H,H}$ = 10.6 Hz, 2 H, 8-H) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 31.9 [$C(CH_3)_3$], 39.1 [$C(CH_3)_3$], 78.9, 79.7 ($C{\equiv}C$), 73.9, 110.6, 124.0, 124.6, 135.7, 138.9, 140.1, 142.4, 145.5, 164.7 (C_{Az}) ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\lg\varepsilon$) = 252 (4.75), 295 (4.75), 313 (4.68) (sh), 388 (4.67), 402 (4.50) (sh), 420 (4.50), 432 (4.45) (sh), 460 (4.47), 603 (3.20), 648 (3.10) (sh), 735 (2.40) (sh) nm. MS (FD): *m*/*z* (%) = 666 (100) [M^{+}]. $C_{32}H_{28}I_2$ (666.4): calcd. C 57.68, H 4.24; found C 57.96, H 4.27.

6-*tert*-Butyl-1,3-bis[(6-*tert*-butyl-3-iodoazulen-1-yl)butadiynyl]azulene (6): **3** and **4** afforded a mixture of **5** (160 mg, 24%) and **6** (197 mg, 22%). **6:** Brown crystals, m.p. 178–180 °C. FT-IR (KBr): $\tilde{\nu}$ = 2961, 2872 (C–H), 2122 ($C{\equiv}C$), 1578, 1362, 838 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.47, 1.48 [2 s, 27 H, $C(CH_3)_3$], 7.53–7.61 (m, 6 H, 5-, 5′-, 7-, 7′-H), 8.01 (s, 2 H, 2′-H), 8.06 (s, 1 H, 2-H), 8.18 (d, $^{3}J_{H,H}$ = 10.6 Hz, 2 H, 4′-H), 8.52–8.59 (m, 4 H, 4-, 8-, 8′-H) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 31.9 [$C(CH_3)_3$], 39.1 [$C(CH_3)_3$], 78.5, 79.0, 79.1, 79.8 ($C{\equiv}C$), 73.9, 109.0, 110.6, 124.0, 124.6, 125.3, 135.7, 136.8, 138.9, 140.1, 142.5, 142.8, 145.7, 164.7 (C_{Az}) ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\lg\varepsilon$) = 243 (4.84), 256 (4.85), 303 (4.92), 320 (4.91), 338 (4.89), 408 (4.64) (sh), 418 (4.77), 450 (4.66) (sh), 607 (3.40), 650 (3.29) (sh) nm. MS (FD): *m*/*z* (%) = 896 (100) [M^{+}]. $C_{50}H_{42}I_2$ (896.7): calcd. C 66.97, H 4.72; found C 67.15, H 4.92.

1-(6-*tert*-Butyl-3-iodoazulen-1-yl)-4-(6-*tert*-butylazulen-1-yl)-1,3-butadiyne (8): **3** and **7** afforded a mixture of **2b**[17] (90 mg, 24%), **5** (179 mg, 27%) and **8** (216 mg, 40%). **8:** Brown crystals, m.p. 128–130 °C. FT-IR (KBr): $\tilde{\nu}$ = 2920, 2852 (C–H), 2185, 2100 ($C{\equiv}C$), 1654, 1560, 1396, 832 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.46 [s, 18 H, $C(CH_3)_3$], 7.21 (d, $^{3}J_{H,H}$ = 4.0 Hz, 1 H, 3-H), 7.43–7.58 (m, 4 H, 5-, 5′-, 7-, 7′-H), 7.94 (d, $^{3}J_{H,H}$ = 3.99 Hz, 1 H, 2-H), 7.99 (s, 1 H, 2′-H), 8.16 (d, $^{3}J_{H,H}$ = 10.4 Hz, 1 H, 4-H), 8.25 (d, $^{3}J_{H,H}$ = 10.3 Hz, 1 H, 4′-H), 8.53 (d, $^{3}J_{H,H}$ = 10.3 Hz, 1 H, 8-H), 8.60 (d, $^{3}J_{H,H}$ = 10.4 Hz, 1 H, 8′-H) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 30.3, 31.9 [$C(CH_3)_3$], 38.9, 39.1 [$C(CH_3)_3$], 78.3, 78.9, 80.0, 80.6 ($C{\equiv}C$), 73.9, 108.7, 110.9, 117.5, 123.1, 123.6, 123.8, 124.4, 135.7, 135.9, 136.7, 138.8, 139.56, 140.0, 140.7, 142.1, 142.3, 145.5, 163.4, 164.6 (C_{Az}) ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\lg\varepsilon$) = 244 (4.68), 296 (4.71), 331 (4.68), 419 (4.50), 430 (4.46) (sh), 458 (4.47), 595 (3.17) nm. MS (FD): *m*/*z* (%) = 540 (100) [M^{+}]. $C_{32}H_{29}I$ (540.5): calcd. C 71.11, H 5.41; found C 71.19, H 5.51.

Tetramer 10: **9** afforded **10** as green crystals (512 mg, 62%), m.p. 194–196 °C. FT-IR (KBr): $\tilde{\nu}$ = 2960 (C–H), 2186, 2124 ($C{\equiv}C$), 1574, 1427, 1353, 1239, 839 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.48, 1.49 [2 s, 36 H, $C(CH_3)_3$], 7.28 (d, $^{3}J_{H,H}$ = 4.0 Hz, 2 H, 3′-H), 7.40 (dd, $^{3}J_{H,H}$ = 10.3 Hz, $^{4}J_{H,H}$ = 1.8 Hz, 2 H, 5′-H), 7.47–7.57 (m, 6 H, 5-, 7-, 7′-H), 8.00 (d, $^{3}J_{H,H}$ = 4.0 Hz, 2 H, 2′-H), 8.12 (s, 2 H, 2-H), 8.25 (d, $^{3}J_{H,H}$ = 10.3 Hz, 2 H, 4′-H), 8.57 (d, $^{3}J_{H,H}$ = 10.3 Hz, 2 H, 8′-H), 8.62–8.69 (m, 4 H, 4-, 8-H) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 31.9, 32.0 [$C(CH_3)_3$], 39.1, 39.3 [$C(CH_3)_3$], 79.4, 89.1, 90.8 ($C{\equiv}C$), 108.7, 110.9, 111.9, 117.6, 122.8, 123.3, 124.9, 125.1, 135.7, 136.6, 136.8, 138.6, 139.9, 140.6, 140.8, 141.3, 142.7, 163.6, 165.7 (C_{Az}) ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\lg\varepsilon$) = 241 (4.86), 291 (4.95), 316 (4.98), 330 (4.99), 411 (4.84), 435 (4.80) (sh), 615 (3.41) nm. MS (FD): *m*/*z* (%) = 826 (100) [M^{+}]. $C_{64}H_{58}$ (827.2): calcd. C 92.93, H 7.07; found C 92.57, H 7.30.

Pentamer 11 and Hexamer 12: **4** and **9** afforded a mixture of **10** (165 mg, 20%), **11** (17%) and **12** (51 mg, 4%). **11:** Deep green crystals, m.p. 205–207 °C. FT-IR (KBr): $\tilde{\nu}$ = 2960, 2928, 2866 (C–H), 2178, 2120 ($C{\equiv}C$), 654, 1353, 837 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 1.48 [s, 18 H, C(CH$_3$)$_3$], 1.49 [s, 18 H, C(CH$_3$)$_3$], 1.50 [s, 9 H, C(CH$_3$)$_3$] 7.25 (d, $^3J_{H,H}$ = 4.1 Hz, 2 H, 3′′-H), 7.40 (dd, $^3J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 1.6 Hz, 2 H, 5′′-H), 7.47–7.62 (m, 8 H, 5-, 5′-, 7-, 7′-, 7′′-H), 8.00 (d, $^3J_{H,H}$ = 4.1 Hz, 2 H, 2′′-H), 8.08 (s, 1 H, 2-H), 8.12 (s, 2 H, 2′-H), 8.25 (d, $^3J_{H,H}$ = 10.3 Hz, 2 H, 4′′-H), 8.54–8.69 (m, 8 H, 4-, 4′-, 8-, 8′-, 8′′-H) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$, 25 °C): δ = 30.3, 30.4 [C(*C*H$_3$)$_3$], 37.3, 37.5 [*C*(CH$_3$)$_3$], 77.1, 77.4, 77.6, 77.7, 87.3, 88.8 (*C*≡*C*), 107.1, 107.6, 109.2, 110.1, 115.8, 120.8, 121.1, 122.7, 122.9, 123.7, 134.0, 134.8, 134.9, 135.2, 137.0, 138.2, 138.7, 139.1, 139.8, 141.0, 141.2, 161.3, 163.2, 163.9 (C$_{Az}$) ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 242 (4.94), 293 (5.06) (sh), 320 (5.12) (sh), 330 (5.13), 409 (5.02), 433 (4.96) (sh), 463 (4.74) (sh), 612 (3.54) nm. MS (ESI): *m*/*z* (%) = 1057 (100) [(M+H)$^+$]. C$_{82}$H$_{72}$ (1057.5): calcd. C 93.14, H 6.86; found C 92.72, H 7.02. **12:** Black crystals, m.p. > 260 °C. FT-IR (KBr): $\tilde{\nu}$ = 2954, 2862 (C–H), 2180, 2122 (C≡C), 1654, 1577, 1354, 839 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 1.48 [s, 18 H, C(CH$_3$)$_3$], 1.49 [s, 36 H, C(CH$_3$)$_3$], 7.28 (d, $^3J_{H,H}$ = 4.0 Hz, 2 H, 3-H), 7.39 (dd, $^3J_{H,H}$ = 10.4 Hz, $^4J_{H,H}$ = 1.7 Hz, 2 H, 5′′-H), 7.48–7.63 (m, 10 H, 5-, 5′-, 7-, 7′-, 7′′-H), 8.05 (d, $^3J_{H,H}$ = 4.0 Hz, 2 H, 2′′-H), 8.08 (s, 2 H, 2′-H), 8.12 (s, 2 H, 2-H), 8.25 (d, $^3J_{H,H}$ = 10.3 Hz, 2 H, 4′′-H), 8.54–8.69 (m, 10 H, 4-, 4′-, 8-, 8′-, 8′′-H) ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 242 (5.05), 298 (5.12) (sh), 329 (5.19), 407 (5.07), 462 (4.84) (sh), 610 (3.63) nm. MS (FD): *m*/*z* (%) = 1287 (100) [(M+H)$^+$]. C$_{100}$H$_{86}$ (1287.8): calcd. C 93.27, H 6.73; found C 93.38, H 6.59.

Pentamer 13 and Octamer 14: 7 and **15** afforded a mixture of **2b** (99 mg, 24%), **13** (211 mg, 20%) and **14** (51 mg, 3%). **13:** Black crystals, m.p. 164–166 °C. FT-IR (KBr): $\tilde{\nu}$ = 2960, 2928, 2856 (C–H), 2186, 2125, 2200 (C≡C), 1577, 1399, 1357, 839 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.48 [s, 18 H, C(CH$_3$)$_3$], 1.50 [s, 18 H, C(CH$_3$)$_3$], 1.51 [s, 9 H, C(CH$_3$)$_3$], 7.23 (d, $^3J_{H,H}$ = 4.0 Hz, 2 H, 3′′-H), 7.44–7.60 (m, 10 H, 5-, 5′-, 5′′-, 7-, 7′-, 7′′-H), 7.97 (d, $^3J_{H,H}$ = 4.0 Hz, 2 H, 2′′-H), 8.14 (s, 2 H, 2′-H), 8.20 (s, 1 H, 2-H), 8.26 (d, $^3J_{H,H}$ = 10.3 Hz, 2 H, 4′′-H), 8.56–8.66 (m, 8 H, 4-, 4′-, 8-, 8′-, 8′′-H) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$, 25 °C): δ = 31.9, 32.0 [C(*C*H$_3$)$_3$], 38.9, 39.1 [*C*(CH$_3$)$_3$], 79.0, 79.1, 79.3, 80.1, 89.1, 89.5 (*C*≡*C*), 108.9, 109.1, 110.9, 111.3, 117.5, 123.1, 123.6, 123.8, 124.3, 124.5, 135.9, 136.2, 136.5, 136.7, 139.6, 140.6, 140.7, 140.8, 141.4, 142.1, 142.5, 163.4, 164.4, 164.8 (C$_{Az}$) ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 242 (4.94), 301 (5.04) (sh), 313 (5.07), 330 (5.07), 344 (5.01), 407 (4.94), 445 (4.82) (sh), 599 (3.48), 698 (3.20) (sh) nm. MS (FD): *m*/*z* (%) = 1056 (100) [M$^+$]. C$_{82}$H$_{72}$ (1057.5): calcd. C 93.14, H 6.86; found C 93.26, H 6.96. **14:** Black crystals, m.p. > 260 °C. FT-IR (KBr): $\tilde{\nu}$ = 2960, 2920, 2856 (C–H), 2174, 2124 (C≡C), 1654, 1576, 1357, 839 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 1.48, 1.50, 1.51, 1.52 [4 s, 72 H, C(CH$_3$)$_3$], 7.23 (d, $^3J_{H,H}$ = 3.9 Hz, 2 H, 3′′′-H), 7.45 (dd, $^3J_{H,H}$ = 10.4 Hz, $^4J_{H,H}$ = 1.7 Hz, 2 H, 5′′′-H), 7.50–7.61 (m, 14 H, 5-, 5′-, 5′′-, 7-, 7′-, 7′′-, 7′′′-H), 7.95 (d, $^3J_{H,H}$ = 4.0 Hz, 2 H, 2′′′-H), 8.13 (s, 2 H, 2′′-H), 8.15 (s, 2 H, 2′-H), 8.20 (s, 2 H, 2-H), 8.25 (d, $^3J_{H,H}$ = 10.3 Hz, 2 H, 4′′′-H), 8.55–8.67 (m, 14 H, 4-, 4′-, 4′′-, 8-, 8′-, 8′′-, 8′′′-H) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$, 25 °C): δ = 31.9 [C(*C*H$_3$)$_3$], 38.9 [*C*(CH$_3$)$_3$], 79.1, 79.2, 79.3, 80.1, 89.1, 89.5 (*C*≡*C*), 108.8, 109.1, 110.9, 111.3, 117.5, 123.1, 123.7, 123.8, 124.4, 124.5, 124.6, 135.9, 136.2, 136.5, 136.7, 139.6, 140.6, 140.8, 141.4, 142.1, 142.5, 142.6, 158.3, 163.4, 164.4, 164.8 (C$_{Az}$) ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 242 (5.12), 301 (5.22) (sh), 314 (5.27), 330 (5.26), 343 (5.22) (sh), 406 (5.13), 610 (3.68) nm. MS (FD): *m*/*z* (%) = 1698.8 (7) [(M+H)$^+$], 849.9 [(M+2 H)$^{2+}$/2]. C$_{132}$H$_{114}$ (1700.4): calcd. C 93.24, H 6.76; found C 93.10, H 6.97.

General Procedure for the Palladium/Copper-Catalyzed Coupling of Ethynylazulenes with Iodoazulenes: To a solution of the appropriate iodoazulenes **5**, **6** or **8** (2 mmol) in triethylamine (TEA) (50 mL), bis(triphenylphosphane)palladium(II) chloride (0.04 mol-%) and CuI (0.08 mol-%) were added. The reaction mixture was stirred at room temp. under N$_2$ for 10 min. The appropriate ethynylazulenes **4** or **7** (1 or 2 equiv.) in TEA (10 mL) were then added slowly over a period of 6 h. The reaction mixture was stirred for further 10 h and filtered through a short column of alumina (B II–III). The solvent was removed in vacuo and the remaining material was purified by chromatography on alumina (B II–III) with CH$_2$Cl$_2$/*n*-hexane (1:4) to give **10**, **11**, and **13**.

Tetramer 10: 5 and **7** afforded **10** (388 mg, 47%).

Pentamer 11: 6 and **7** afforded **11** (391 mg, 37%).

Pentamer 13: 8 and **4** afforded **13** (348 mg, 33%).

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