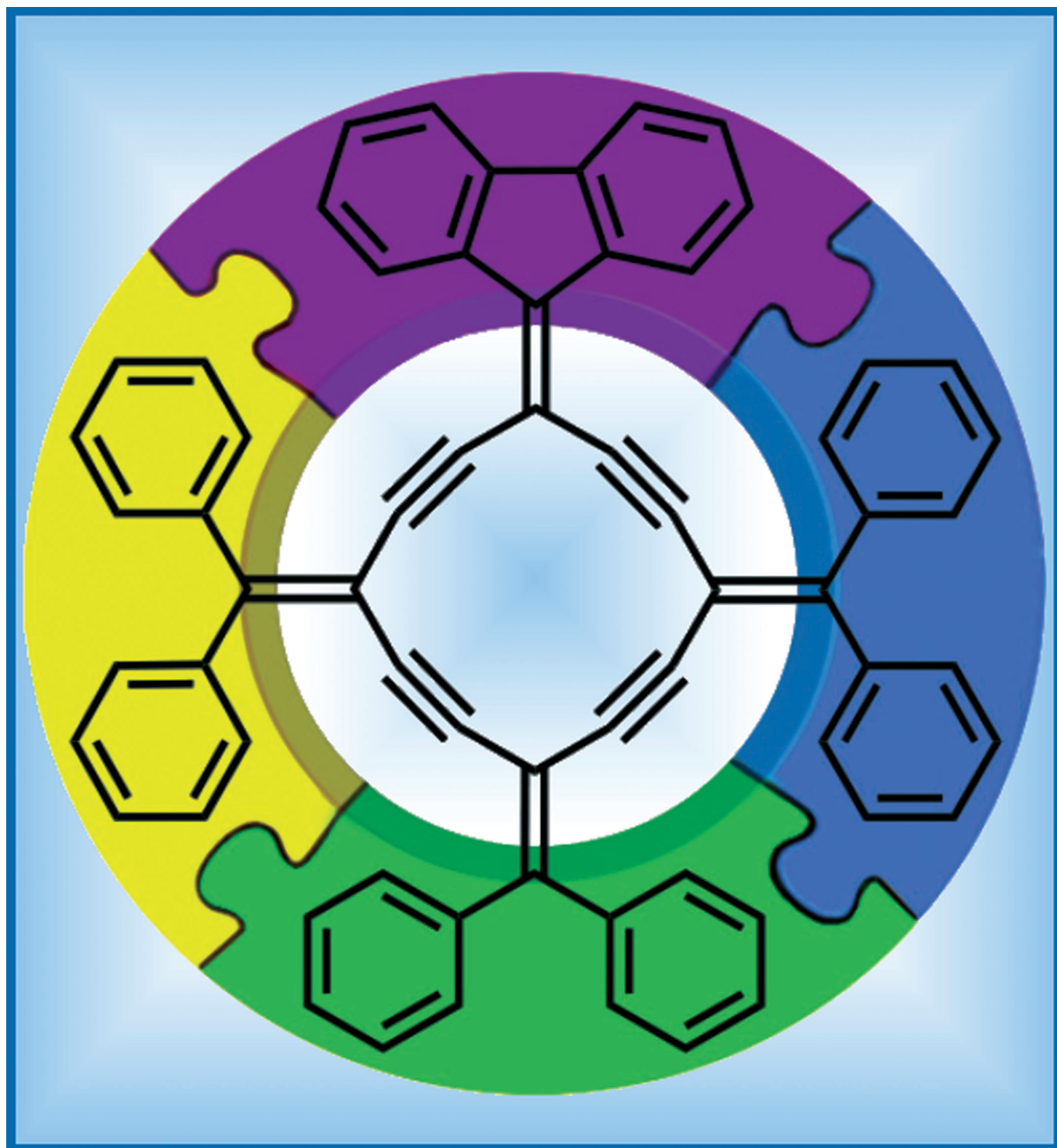


Synthesis and Derivatization of Expanded [n]Radialenes ($n = 3, 4$)

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Abstract: Versatile, iterative synthetic protocols to form expanded $[n]$ radialenes have been developed ($n=3$ and 4), which allow for a variety of groups to be placed around the periphery of the macrocyclic framework. The successful use of the Sonogashira cross-coupling reaction to complete the final ring closure demonstrates the ability of this reaction to tolerate significant ring

strain while producing moderate to excellent product yields. The resulting radialenes show good stability under normal laboratory conditions in spite of their strained, cyclic structures. The

Keywords: cross-conjugation • cross-coupling • macrocycles • radialenes • strained molecules

physical and electronic characteristics of the macrocycles have been documented by UV-visible spectroscopy, electrochemical methods, and X-ray crystallography (four derivatives), and these studies provide insight into the properties of these compounds as a function of pendent substitution in terms of conjugation and donor/acceptor functionalization.

Introduction

It is hard to debate the potential role of carbon-rich organic molecules and materials as the active components in electronic, optical, and optoelectronic devices. The commercial release of a 55-inch organic light-emitting diode (OLED) TV was announced earlier this year,^[1] graphene offers an intriguing and realistic alternative to indium tin oxide (ITO) for flexible transparent electrodes,^[2] and the fullerene derivative phenyl- C_{61} -butyric acid methyl ester (PCBM) is by far the most common electron acceptor in polymer solar cells,^[3] just to name a few. Although the applications of carbon-rich molecules might be the crowning jewels of years of research, it is arguably the fundamental study of new molecular designs and structures that often make these headline discoveries possible.

Conjugated macrocycles are just one small section of the general class of carbon-rich molecules.^[4] In addition to their aesthetically appealing structures, conjugated macrocycles offer a rigid structure that has often been used to study aromaticity,^[5] and their defined geometry provides supramolecular building blocks toward, for example, materials with solid-state porosity.^[6] Radialenes (**1**; Figure 1) are a particular class of carbon-rich macrocycles that have drawn attention on account of their interesting structure and unusual electronic properties.^[7] Expanded radialenes, on the other

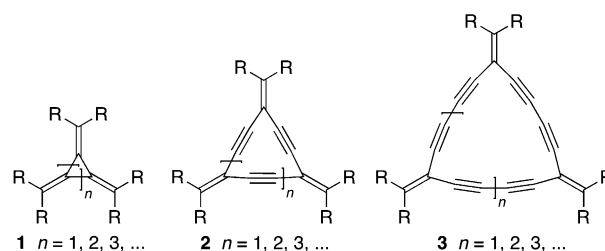


Figure 1. General structure of $[n]$ radialenes (**1**) and expanded $[n]$ radialenes (**2** and **3**).

hand, are macrocycles that arise from the formal insertion of acetylenic spacers into the cyclic, all-carbon core of a radialene, as in **2** and **3**.^[8] Like other acetylenic macrocycles such as the perethynylated dehydroannulenes (DHAs)^[9] and radiannulenes (RAs),^[10] expanded radialenes are two-dimensionally conjugated by virtue of a combination of linear and cross-conjugated pathways.^[11–13]

Expanded radialenes with the general structure **3** have been explored primarily by Diederich and co-workers.^[14] Based on the elegant use of tetraethynylethene building blocks, the assembly of derivatives with both fundamental and applied utility have been accomplished.^[15,16] There remains, however, only two reports of compounds from the class of expanded radialenes **2**, which are made up of alternating enyne segments. The most recent report describes the synthesis of symmetrical derivatives with phenyl rings as substituents **2a–d** (Figure 2),^[17] whereas the other study outlines the synthesis of a single example, the expanded [6]radialene **4**, which is decorated with an alternating sequence of isopropylidene and cyclohexylidene substituents.^[18] In fact, macrocycle **4** remains, to our knowledge, the only expanded radialene selectively assembled in which all of the alkylidene substituents are not identical.^[19] Unfortunately, radialene **4** was disappointingly unstable under ambient conditions, likely the result of an oxygen ene reaction at the allyl position as a result of the alkyl substituents.^[20] Members of the series of perphenylated radialenes (**2a–d**), on the other hand, are reasonably thermally stable, and they show little degradation in the presence of light, air, or moisture. The synthesis of **2a–d** and **4** arises from a similar iterative process based on the use of three main building blocks: the ene-

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201302452>.

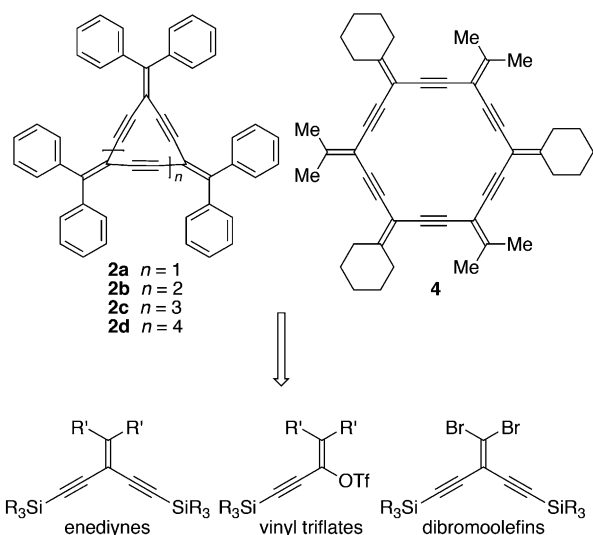
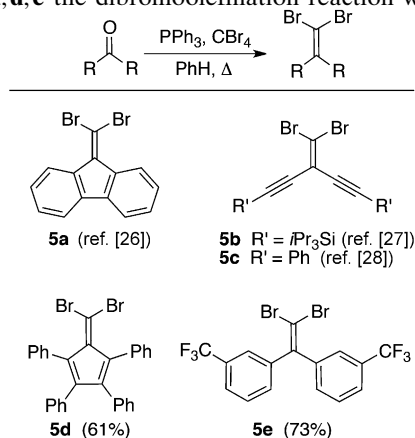


Figure 2. Building blocks for enyne radialene synthesis.

diynes, vinyl triflates, and dibromoolefins shown in Figure 2. These three building blocks, when combined with our previous methodology developed for the synthesis of cross-conjugated enyne oligomers from vinyl triflates (the *iso*-polydiacetylenes (*iso*-PDAs)),^[20–23] suggest a viable route to enyne radialenes with more diverse substitution patterns. We report herein our efforts to develop the modular synthesis of expanded [*n*]radialenes, as well as characterization of these products by spectroscopic, electrochemical, and solid-state structural analyses.

Results and Discussion

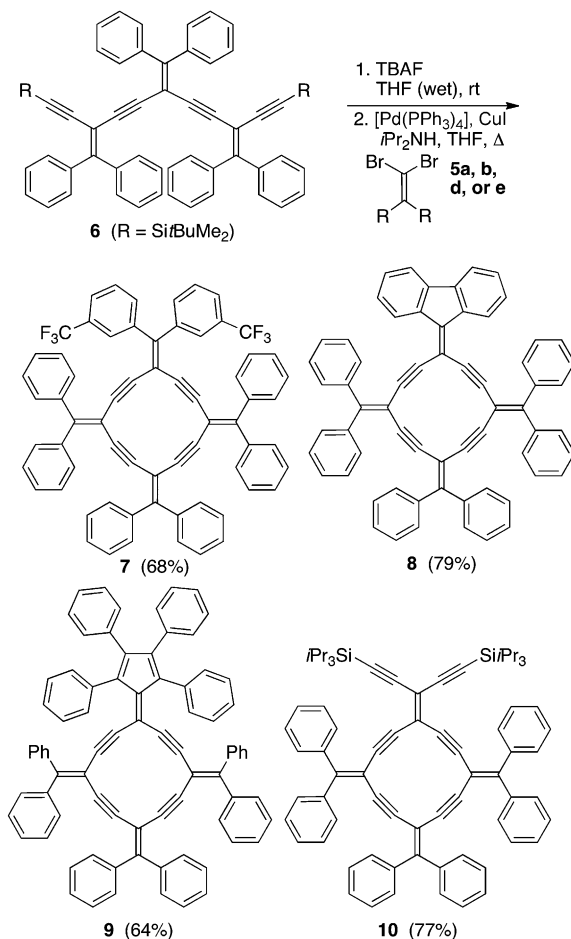
As described above, dibromoolefins are important building blocks toward the synthesis of expanded radialenes. To this end, **5a–e** were synthesized by means of the Ramirez protocol^[24] from the corresponding ketones by using PPh₃ and CBr₄ (Scheme 1). Compounds **5a–c** were formed as previously reported,^[25–27] whereas the synthesis of **5d** and **5e** was developed for the present study. It is noteworthy that in the case of **5a, d, e** the dibromoolefination reaction was sluggish



Scheme 1. Synthesis of dibromoolefins **5a–e**.

due to steric hindrance about the ketone carbon, and the reactions were thus best conducted under reflux conditions in benzene.

The formation of mono-substituted expanded [4]radialenes rested on *iso*-PDA **6** as the common precursor (Scheme 2), and this cross-conjugated precursor was readily



Scheme 2. Synthesis of expanded [4]radialenes **7–10** (yields given are over the two steps from **6**).

available from a known procedure.^[23] Subjecting **6** to tetra-*n*-butylammonium fluoride (TBAF) in THF at room temperature cleanly gave the desilylated *iso*-PDA. Because of the limited stability of the terminal acetylene product, it was taken directly to the subsequent Sonogashira cross-coupling reaction with a dibromoolefin conducted in THF under reflux conditions.^[28] The reactions to form **7–10** were monitored by thin-layer chromatography (TLC), which showed that progress was no longer observed after about 18 h. Once judged completed, a standard aqueous workup and column chromatography gave the desired products. Following this protocol, aryl derivatives **7** and **8** were isolated as bright yellow solids in good yields (68 and 79%, respectively), whereas the fulvene-like derivative **9** was obtained as a brown solid and in slightly lower yield (64%), presumably

due to the sensitivity of the cross-coupling reaction to the sterically encumbered environment of the dibromoolefin moiety. Finally, the reaction with dibromoolefin **5b** gave expanded [4]radialene **10** in 77% yield as a yellow solid. The successful formation of **10** in good yield is noteworthy because it opens the door to postsynthetic modification of the expanded [4]radialene skeleton by following a sequence of desilylation and Sonogashira reaction (see below).

A single crystal of radialene **9** suitable for X-ray crystallographic analysis was grown in THF at 4–5 °C (Figure 3). The macrocyclic framework of **9** is clearly strained, with acetylenic bond angles spanning from 164.14(18)° for C6–C7–C8 to 170.70(18)° for C3–C4–C5. This structure is, however, consistent with that reported for perphenylated expanded [4]radialene **2b**.^[17] Unlike **2b**, which is planar, the steric demands of the tetraphenylcyclopentadienylidene group have a dra-

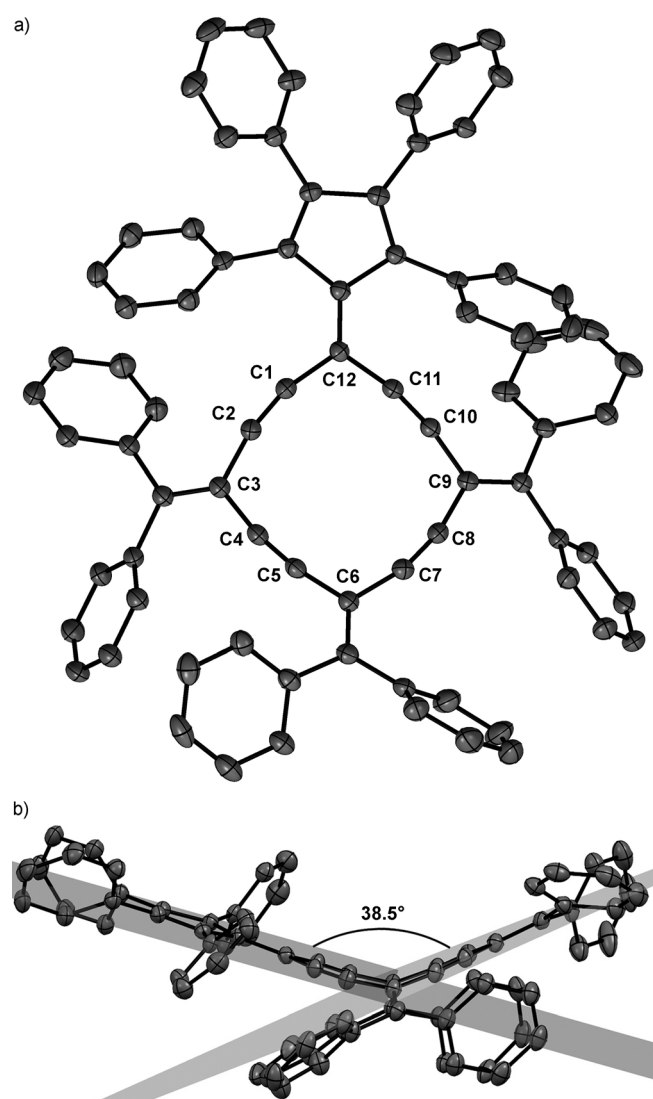
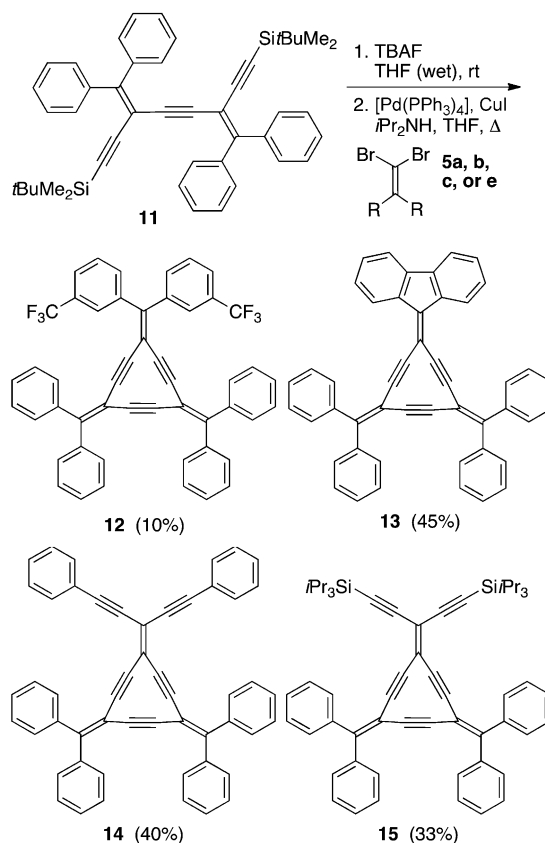


Figure 3. a) ORTEP drawing of expanded [4]radialene **9** (hydrogen atoms and cocrystallized THF solvent molecule removed for clarity), and b) side-on view of **9** illustrating puckering of the radialene skeleton (ORTEPs shown at 30% probability).

matic effect on the planarity of radialene **9**. As shown in Figure 3b, steric repulsion between phenyl rings leads to a puckering of the ring system (38.5°), similar to that found for cyclobutane.

The syntheses of the smallest members of the expanded [n]radialene series were then targeted, namely, the expanded [3]radialenes shown in Scheme 3. This required the syn-



Scheme 3. Synthesis of expanded [3]radialenes **12–15** (yields given are over the two steps from **11**).

thesis of *iso*-PDA dimer **11**, which was achieved by using the reported literature procedure.^[23] With **11** in hand, a sequence of desilylation using TBAF and Sonogashira cross-coupling with dibromoolefins **5a–c, e** gave the desired expanded radialene products **12–15** in a manner similar to that developed for [4]radialenes **7–10**. Despite their strained acetylenic framework, the [3]radialene products **12–15** showed no particular instability under normal laboratory conditions, and they could be purified by column chromatography to give the products as yellow or orange solids. The isolated yields for **12–15** were substantially lower over the two steps from **11** than those of the analogous cyclic tetramers **7–10**. This is likely a result of the rather significant strain incorporated into the conjugated structure during the final ring-closing event, as well as, in the case of **12**, the steric demands of the dibromoolefin **5e**^[23] (relative to the less hindered **5a–c**). The successful formation of **12–15**, however, offers an excit-

ing testament to the ability of the Sonogashira cross-coupling reaction to tolerate significant ring strain on the way to forming interesting macrocyclic structures.^[29]

Single crystals of expanded [3]radialene **14** were grown from a mixture of acetone and dichloromethane maintained at a temperature of 4–5°C. The most notable parameters from the solid-state structure of **14** (Figure 4) are the planar

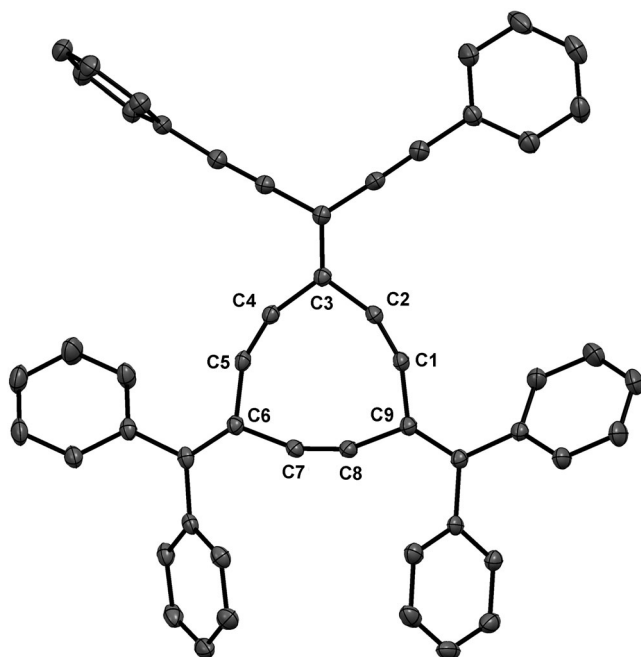


Figure 4. ORTEP drawing of expanded [3]radialene **14** (ORTEP shown at 30% probability; hydrogen atoms removed for clarity).

radialene skeleton and the alkyne bond angles found for C4–C5–C6 at 155.59(14)°, C1–C2–C3 at 156.20(15)°, and C2–C1–C9 at 156.30(15)°. These are amongst the smallest alkyne angles characterized by X-ray crystallography to date.^[30] Finally, it is interesting to note the difference in twist angles of the two phenyl groups appended to the tetraethynylethene (TEE) section of **14**. In one case, the phenyl ring is almost coplanar with the enyne skeleton of the radialene (15°) to

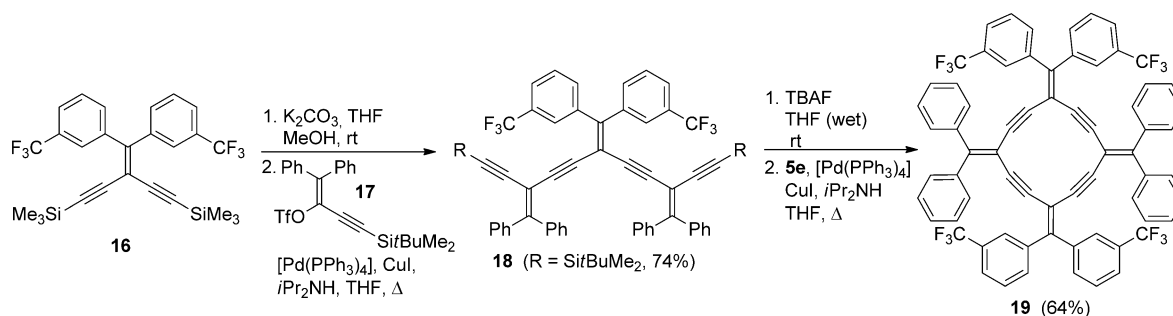
permit π -conjugation, and it is severely twisted (79°) in the other case.^[31]

Further functionalization of the radialene core was available through selective use of enediyne and dibromoolefin building blocks to assemble *iso*-PDAs with varied structures. As described in Scheme 4, this goal was readily achieved through derivatization of enediyne **16** by using a sequence of desilylation and subsequent Sonogashira coupling with vinyl triflate **17**.^[23] *iso*-PDA **18** was thus formed in good yield, and then carried on to the synthesis of the C₂-symmetric [4]radialene **19** by means of desilylation with TBAF and cross-coupling with **5e**. The disubstituted expanded [4]radialene **19** was isolated as a bright yellow solid that is stable under ambient conditions.

Single crystals of **19** suitable for crystallography were grown by the diffusion of pentane into a solution of **19** in chloroform at 4–5°C. The centrosymmetric framework of the radialene is practically planar (Figure 5), including exocyclic alkyldiene carbon atoms C3/C3', whereas the alkyldiene carbon atoms C7/C7' lie 0.33 Å above/below this plane.^[32] The acetylenic bonds angles fall in a narrow range that spans from 167.85(18)° for C1–C8–C6 to 170.63(18)° for C4–C5–C6. The two CF₃C₆H₄ rings are rotated by approximately 43 and 81° from the plane of the radialene, whereas the phenyl rings are twisted by 43–46°.

Finally, the protocol developed for **19** was easily adapted to the formation of the analogous system with two tetraethynylethene units (Scheme 5). In this case, the trimethylsilyl group of enediyne **20** was carefully removed to give **21**, which was then utilized in a cross-coupling reaction with dibromoolefin **5b** to give *iso*-PDA **22**. With **22** in hand, a second iteration of desilylation and cross-coupling with **5b** gave the radialene **23** as a stable yellow solid (m.p. 235°C) in excellent yield of 78% over the two steps from **22**.

Single crystals for X-ray analysis were grown from a solution of **23** in CHCl₃ at 4–5°C; the ORTEP plot of radialene **23** is shown in Figure 5. Overall, bond lengths and angles for the centrosymmetric structure are unremarkable in comparison to the structures of expanded [4]radialenes **2b**, **9**, and **19** as described earlier. The framework of **23** is slightly twisted, with alkyldiene carbon atoms C4/C4' that lie approximately 0.4 Å out of a plane generated from the twelve carbon atoms of the radialene core. This twisting also forces the



Scheme 4. Synthesis of C₂-symmetric expanded [4]radialene **19** (yields of **18** and **19** are over the two steps from **16** and **18**, respectively).

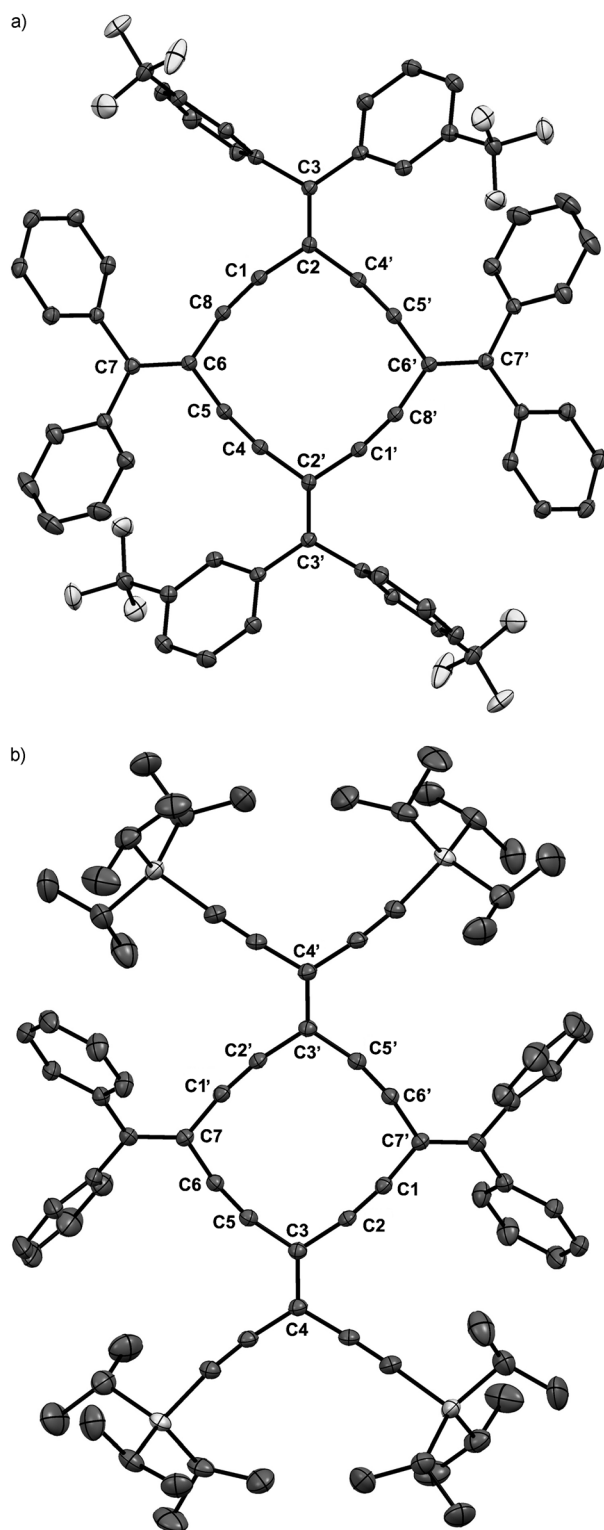


Figure 5. ORTEP drawings of a) **19** and b) **23** (ORTEPs shown at 30% probability; hydrogen atoms removed for clarity).

pendent alkyne units to positions slightly above and below this plane, although the deviation is not particularly significant (see the Supporting Information).

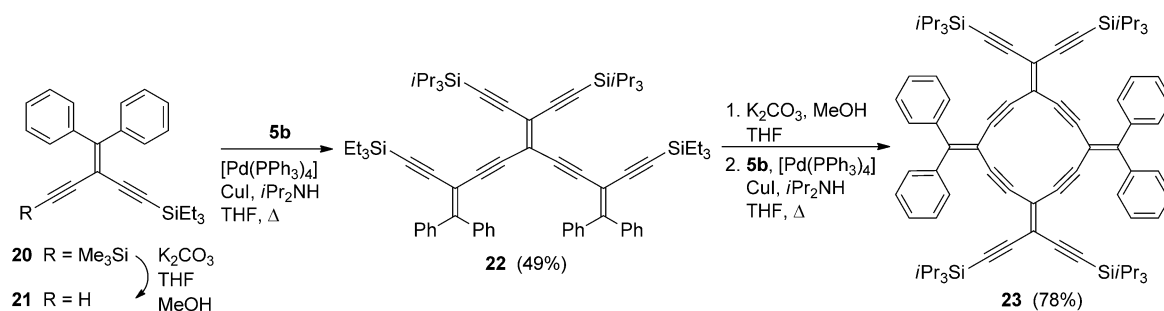
A final question to be answered in this study was the prospect of postsynthetic modification of the radialene

framework, such as desilylation of expanded [4]radialene **10** followed by Sonogashira cross-coupling to an aryl iodide (Scheme 6). Thus, removal of the triisopropylsilyl groups of **10** was effected by treatment with TBAF (2.2 equiv) at 0°C, and this reaction proceeded without significant decomposition. After the removal of the triisopropylsilyl groups, attempts to introduce aryl groups by means of Sonogashira cross-coupling at room temperature resulted in long reaction times and the formation of numerous byproducts that complicated purification. When the analogous reactions were carried out under reflux conditions, however, the situation improved dramatically and the desired radialenes **24–26** were obtained in 75–94% yield after purification by either column chromatography or recrystallization.

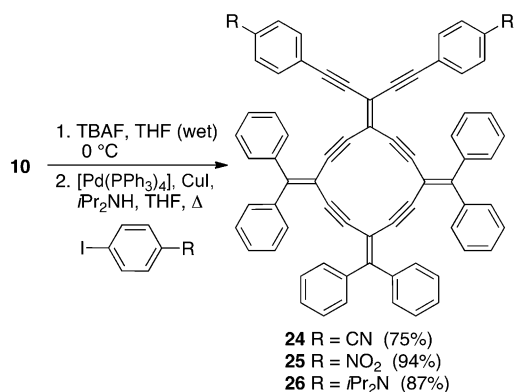
Although the primarily goals of this study were concerned with the development of efficient synthetic protocols, some comments on the physical properties of these new and rather unique molecules are also worth noting. Thus, in addition to X-ray crystallographic analysis of **9**, **14**, **19**, and **23** as described above, all new radialenes were also characterized by typical spectroscopic methods to confirm their structure (see the Experimental Section and the Supporting Information), as well as by UV-visible spectroscopy and electrochemical methods to provide a preliminary overview of their electronic characteristics (spectra and electrochemical traces are provided in the Supporting Information).

UV-visible spectroscopy in solution gives an empirical picture of changes in the electronic structure as a function of pendent substituents (Table 1). Salient points of this analysis include the following observations:

- 1) The spectra of all the radialenes show a strong absorption in the higher-energy range from 363 nm (e.g., **2a** and **12**) to approximately 400 nm (e.g., **9**, **23–26**).
- 2) UV-visible spectra for expanded [3]radialenes typically show more resolved signals than the [4]radialenes. This is likely the result of the centrosymmetric (**2b**, **19**, **23**) or pseudo-centrosymmetric structure (**7–10**, and to a lesser extent **24–26**) of the [4]radialenes and the resulting selection rules.^[33] For example, CF₃-substituted [3]radialene **12** shows strong, defined absorptions at 363 and 412 nm, whereas [4]radialenes **7** and **19** both show a similar high-energy absorption (376 nm) but only a weak absorption at lower energy (\approx 430 nm, shoulder). A similar observation can be found for the series of triisopropylsilylethynyl-substituted radialenes, **10**, **15**, and **23**.
- 3) Switching from aryl alkylidene substitution (**2a/2b** or **7/12**) to the cyclic fluorenylidene (**8/13**) affords a significant redshift in λ_{max} , as the pendent aryl rings of the latter are formally made coplanar with the radialene skeleton through annulation of the aryl rings. This trend has been previously observed for radiaannulenes.^[10d]
- 4) As expected, the largest changes in λ_{max} are found in derivatives with pendent groups that extend π -conjugation beyond the radialene core, including the fluorenylidene (**8** and **13**), the tetraphenylcyclopentadienyl (**9**), and phenylethynyl (**14**) moieties. The contribution of the tri-



Scheme 5. Synthesis of expanded [4]radialene **23** (yields of **22** and **23** are over the two steps from **20** and **22**, respectively).



Scheme 6. Postsynthetic modification of expanded [4]radialene **10** (yields given are over the two steps from **10**).

sopropylsilylethynyl substituents (**10**, **15**, **23**) to the π -systems is less dramatic.

- 5) The addition of π -acceptors and π -donors in radialenes **24–26** has the expected effect of decreasing the energy of λ_{max} , especially in the case of **26**, which features the diisopropylaniline donors.

Electrochemical analysis by Osteryoung square-wave and cyclic voltammetry were used to complement analysis of the electronic properties determined by UV-visible spectroscopy. The [4]radialenes show two one-electron oxidative steps, except for **7** and those decorated with the electron-deficient triisopropylsilylethynyl groups (**10** and **23**).^[34] The first oxidative step is reversible for **2b**, **8**, and **10**, and irreversible for the other [4]radialenes. The [4]radialenes in general show two or three reduction events (except **25**), and the first reduction potential is reversible in all cases except for **7** and **25**. All substituted [4]radialene derivatives are easier to reduce than **2b**, whereas the value of first oxidation potential of each radialene relative to **2b** is dependent on the electron-donating or -accepting nature of the pendent substituents.

Expanded [3]radialenes **2a** and **12–15** generally exhibit similar electrochemical behavior to the analogous [4]radialenes. All [3]radialenes except **12** show two one-electron oxidative steps, and the first oxidative step is reversible for **2a**, **13**, and **15**, but it is irreversible for **12** and **14**. All of the ex-

panded [3]radialenes studied exhibit three one-electron reductive steps, and the first reduction event is reversible except for **12**. In comparison to the parent radialene **2a**, the first oxidation potentials of **12–15** are rendered more difficult, especially through either the presence of electron-deficient CF₃ groups or through the extension of the acetylenic scaffold by means of addition of the pendent ethynyl groups. On the other hand, the initial reduction potential for [3]radialenes **13–15** is dramatically lower than **2a**, thus highlighting the influence of the fluorenylidene and ethynyl substituents on the electronic makeup of the radialene framework, particularly for the increase in electron-accepting ability brought on by attachment of the phenylethynyl groups of **14**. Perhaps most surprising is the fact that the two CF₃ substituents in **12** do not appreciably shift the reduction potentials anodically relative to **2a**.

There are several observable trends based on comparisons amongst all derivatives that have been studied (Table 2):

- 1) For radialenes with analogous substituents, **2a/2b**, **8/13**, and **10/15** there is little variance in either the first reduction or oxidation potential on the basis of radialene size. Thus, ring strain does not appear to play a significant role in dictating redox behavior.
- 2) Likewise, the greater degree of functionalization for **23** has little effect on the first initial redox events ($\text{ox}_1 = 0.95$ V and $\text{red}_1 = -1.61$ V), which are essentially the same as that measured for **10** and **15**.
- 3) The outlier to general oxidation trends seems to be **7**, which shows a remarkably facile first oxidation potential (0.79 V) in comparison to both **12** and **19** (both at 0.93 V). Equally puzzling is the fact that the first reduction of **12** ($\text{red}_1 = -1.87$ V) comes at a surprising similar potential compared to **2a** ($\text{red}_1 = -1.9$ V), in spite of the increased electron deficient substitution of the former. On the other hand, reduction of **7** ($\text{red}_1 = -1.79$ V) and **19** ($\text{red}_1 = -1.8$ V) occurs more readily than **12**. The origin of this strange behavior is currently not understood.
- 4) The facile reduction of **8** and **13** also deserves comment, and these results are nicely in line with that reported by Iyoda and co-workers for fluorenylidene-substituted radialenes,^[35] which suggests that this reduction occurs at the electron-accepting cyclopentadienyl moiety.

Table 1. Selected UV/Vis spectroscopic details for expanded [3]- and [4]radialenes.

No.	Absorption energies [nm] (ϵ [M ⁻¹ cm ⁻¹])	Absorption cutoff [nm] ((eV)) ^[a]	HOMO–LUMO gap [eV] ^[b]
2b ^[c,d]	415 (25 500) 377 (99 300)	475 (2.61)	2.71
7 ^[e]	430 (sh; 21 000) ^[e] 376 (81 800)	470 (2.64)	2.58
8 ^[e]	470 (sh; 15 000) ^[e] 393 (86 500)	505 (2.46)	2.34
9 ^[e]	455 (sh; 10 000) ^[e] 403 (20 600)	550 (2.25)	1.91
10 ^[e]	430 (sh; 19 100) ^[e] 388 (47 500)	480 (2.58)	2.50
2a ^[c,d]	415 (107 500) 364 (105 300)	470 (2.64)	2.72
12 ^[e]	412 (18 800) 363 (19 200)	475 (2.61)	3.23
13 ^[e]	474 (12 000) 383 (16 100)	505 (2.46)	2.43
14 ^[e]	482 (27 000) 388 (35 100)	520 (2.38)	2.34
15 ^[e]	450 (sh; 23 300) ^[e] 430 (31 800) 378 (42 800)	495 (2.50)	2.53
19 ^[e]	430 (sh; 35 000) ^[e] 376 (122 000)	465 (2.67)	2.73
23 ^[e]	430 (sh; 16 000) ^[e] 399 (25 500)	480 (2.58)	2.56
24 ^[f]	498 (sh; 13 200) ^[e] 401 (76 800)	560 (2.21)	2.30
25 ^[f]	497 (sh; 13 700) ^[e] 402 (66 800)	580 (2.14)	2.24
26 ^[f]	542 (32 400) 495 (31 700) 401 (71 000)	610 (2.03)	2.07

[a] As was estimated from the intercept of a tangent line to the lowest energy absorption of the UV-visible spectrum with the *x* axis. [b] As was estimated from cyclic voltammetry, $E_{\text{ox1}} - E_{\text{red1}}$. [c] Spectrum acquired in THF. [d] Values taken from Ref. [17]. [e] Estimated by assuming that the observed shoulder (sh) absorption has a Gaussian shape. [f] Spectrum acquired in CH₂Cl₂.

- Radialene **9** shows a notably low-value first reduction potential (red₁ = −1.26 V), likely dominated by the cyclopentadienyl group directly appended to the radialene framework.
- For radialenes **24–26**, the values found for first oxidation and reduction potentials are determined predominantly by donor or acceptor aryl groups appended to the radialene, which has been observed in numerous similar systems.^[36]
- Finally, it is important to note the rather strong correlation between the HOMO–LUMO gaps determined by electrochemical methods and those estimated from the UV-visible absorption spectra (Table 1).

Conclusion

By using a combination of building blocks based on enediynes, vinyl triflates, and dibromoolefins, ten new expanded

[3]- and [4]radialenes have been constructed with a Sonogashira cross-coupling as the final, ring-closing step. The synthesis of expanded [3]radialenes is especially noteworthy in that it clearly demonstrates that the Sonogashira reaction is suitable for constructing strained, conjugated macrocyclic systems. When using [4]radialene **10**, desilylation and subsequent Sonogashira coupling confirms that postsynthetic modification of the radialene skeleton can be quite successful, thereby providing donor or acceptor radialenes **24–26** in good to excellent yield. X-ray crystallographic analysis of four derivatives was used to confirm that the [3]- and [4]radialenes are predominantly planar molecules, although sterically demanding groups can be accommodated through deformation of the planar structure, as observed in [4]radialene **9**. UV-visible spectroscopy and electrochemistry show that the electronic effects based on pendent substituents follow patterns that can be generally explained by expected paradigms with regard to the extension of the conjugated framework and/or the electron-donating or -accepting potential of the group.

Experimental Section

General: Reagents were purchased in reagent grade from commercial suppliers and used without further purification. THF was distilled from sodium benzophenone ketyl. Anhydrous MgSO₄ was used as the drying agent after aqueous workup. Filtration, evaporation, and concentration under vacuum were done at water aspirator pressure. All reactions were performed in standard dry glassware under an inert atmosphere of argon. Column chromatography: silica gel (230–400 mesh). Thin-layer chromatography: precoated plastic sheets covered with 0.20 mm silica gel with fluorescent indicator UV 254 nm; visualization by UV light or KMnO₄ stain. Melting points are uncorrected. Aqueous workup for reactions refers to the following general procedure: Et₂O (5–25 mL) and saturated aqueous NH₄Cl (5–15 mL) were added to the reaction mixture at room temperature. The organic phase was separated and washed successively with saturated aqueous NH₄Cl (2 × 25 mL) and saturated aqueous NaCl (2 × 25 mL), then dried over MgSO₄ and filtered.

¹H, ¹³C, and ¹⁹F NMR spectra were collected at 27 °C in CDCl₃, CD₂Cl₂, or C₂D₂Cl₄; solvent peaks as reference. Coupling constants are reported as observed (±0.5 Hz). For simplicity, the coupling constants of the aryl protons for *para*-substituted aryl groups have been reported as pseudo-first-order (i.e., doublets), even though they are second-order (AA'XX') spin systems. UV/Vis spectra were acquired at RT using a Varian Cary 400 Scan spectrometer. The shape of shoulder absorptions in the spectra are approximated to be Gaussian curves, and the value of both the λ_{max} for the absorption and molar absorptivity were estimated on the basis of this approximation. For mass spectral analyses, low- and high-resolution data are provided in cases when *M*⁺ was not the base peak. Otherwise, only high-resolution data are provided. The samples for ESI mass spectrometry were dissolved in CH₂Cl₂ and made use of a 3:1 MeOH/toluene mixture as the carrier solvent. MALDI mass spectrometry used the matrix *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldiene]malononitrile (DCTB). Differential scanning calorimetry (DSC) measurements were carried out using a Perkin–Elmer Pyris 1 DSC instrument. All thermal analyses were carried out under a flow of nitrogen with a heating rate of 10 °C min⁻¹. Melting points from DSC analysis are reported as the peak maxima, except in cases when the sample decomposed, in which case the onset temperature of the decomposition exothermic peak is reported, as well as the exothermic maxima that correspond to the decomposition. Cyclic voltammetry and Osteryoung electrochemical analyses were generally performed in CH₂Cl₂ that contained 0.1 M of NBu₄PF₆ as the supporting electrolyte. The concentration in analyte was about 5 ×

Table 2. Selected electrochemical data for expanded [3]- and [4]radialenes (values in V).

	E_p ox ₁	$E_{1/2}$ ox ₁	E_p ox ₂	E_p red ₁	$E_{1/2}$ red ₁	E_p red ₂	$E_{1/2}$ red ₂	E_p red ₃
2b ^[a,b]		0.81	1.01		-1.9	-2.16		
7 ^[a]	0.79			-1.79		-2.02		
8 ^[a]		0.83	1.01		-1.51		-1.81	-2.37
9 ^[a]	0.65		0.83		-1.26		-1.54	-1.69 ^[c]
10 ^[a]		0.92			-1.58	-1.88		
2a ^[a,b]		0.82	1.11		-1.90	-2.12		-2.25
12 ^[a]	0.93			-1.87		-2.13		-2.37
13 ^[a]		0.88	1.13		-1.55	-1.88		-2.03
14 ^[a]	0.92		1.16		-1.42	-1.80		-1.89
15 ^[a]		0.94	1.19		-1.59	-1.98		-2.2
19 ^[a]	0.93		1.14		-1.80		-2.01	-2.42
23 ^[a]	0.95				-1.61		-1.85	-2.11
24 ^[d]	0.84		1.06		-1.46		-1.77	
25 ^[d]	0.86		1.09	-1.38				
26 ^[d]	0.32		1.01		-1.75		-2.15	

[a] Performed in CH₂Cl₂ containing 0.1 M of NBu₄PF₆ as the supporting electrolyte. The concentration in analyte was about 5 × 10⁻⁴ M. A 2 mm diameter glassy carbon disk was used as the working electrode and a Pt wire as the counter electrode. A silver wire served as a pseudo-reference electrode. [b] Values from Ref. [17]. [c] $E_{1/2}$. [d] Performed in deoxygenated CH₂Cl₂ containing 0.1 M of NBu₄PF₆ as the supporting electrolyte. The concentration in analyte was about 1 × 10⁻³ M. A 3.2 mm-diameter Pt disk was used as the working electrode, a Pt coil as counter electrode, and a Ag/Ag⁺ pseudoreference electrode was used (0.01 M AgNO₃, 0.1 M Bu₄NPF₆ in CH₃CN). Fc⁺/Fc couple used as internal reference in all cases.

10⁻⁴ M. A 2 mm diameter glassy carbon disk was used as the working electrode and a platinum wire as the counter electrode; Fc⁺/Fc reference. A silver wire served as a pseudo-reference electrode. Cyclic voltammetry for compounds **24–26** was performed in deoxygenated CH₂Cl₂ that contained 0.1 M of Bu₄NPF₆ as the supporting electrolyte. The concentration in analyte was about 1 × 10⁻³ M. A 3.2 mm-diameter Pt disk was used as the working electrode with a Ag/Ag⁺ pseudoreference (0.01 M AgNO₃). A Pt coil served as the counter electrode; Fc⁺/Fc reference. Peak potential, E_p , for irreversible waves and quasireversible waves was estimated as $E_p = (E_{peak} + E_{onset})/2$, whereas that of reversible waves was calculated as $E_{1/2} = (E_{pa} + E_{pc})/2$. By using a scan rate of 150 mV, waves that possess peak widths similar to that of the Fc⁺/Fc, that is, 90–100 mV, and peak heights that have a ratio of approximately 1:1, have been designated reversible. If, however, the ratio of peak heights is 1:1, but peak widths are greater than that of Fc⁺/Fc (90–100 mV), then the waves are designated quasireversible. The electrochemical HOMO–LUMO gap is taken as the absolute value of ($E_{ox1} - E_{red1}$).

Compound 5d: CBr₄ (4.4 g, 13 mmol) was added to a mixture of PPh₃ (6.8 g, 26 mmol) in dry benzene (30 mL), and the resulting mixture was stirred at room temperature for 4 d. Tetraphenylcyclopentadienone (2.0 g, 5.2 mmol) was added in one portion, and the resulting mixture was heated to reflux for 4 h followed by stirring at room temperature for 2 d. The crude reaction product was filtered, and the residue washed with benzene (40 mL). Solvent removal and purification by column chromatography (aluminum oxide (activity level II), hexanes) afforded **5d** (1.7 g, 61%) as an orange solid. $R_f = 0.23$ (hexanes/CH₂Cl₂ 8:1); m.p. 73 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.26$ –7.18 (m, 10H), 6.98–6.93 (m, 6H), 6.81–6.79 ppm (m, 4H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 146.3$, 146.2, 136.6, 134.6, 134.5, 131.5, 129.8, 127.9, 127.1, 126.9, 126.6, 104.1 ppm; IR (CH₂Cl₂, cast): $\tilde{\nu} = 3076$, 3059, 3024, 1520 cm⁻¹; HRMS (EI): m/z calcd for C₃₀H₂₀⁷⁹Br₂: 537.9931 [M^+]; found: 537.9929.

Crystal data for 5d: C₃₀H₂₀Br₂, $M_r = 540.28$; crystal dimensions 0.42 × 0.30 × 0.26 mm; monoclinic space group $P2_1/c$ (no. 14); $a = 18.8242(11)$, $b = 12.7615(7)$, $c = 20.4597(11)$ Å; $\beta = 108.1070(10)^\circ$; $V = 4671.5(5)$ Å³; $Z = 8$; $\rho_{calcd} = 1.536$ g cm⁻³; $\mu = 3.486$ mm⁻¹; $\lambda = 0.71073$ Å; $T = -80$ °C; $2\theta_{max} = 52.78^\circ$, total data collected = 35 548; $R_1(F) = 0.0391$ (7031 observations [$F^2 \geq 2\sigma(F^2)$]); $wR_2(F^2) = 0.1072$ for 577 variables and 9548 unique

data; residual electron density = 1.230 and -0.606 e Å⁻³. An ORTEP drawing of **5d** is found in the Supporting Information.

Compound 5e: CBr₄ (10.9 g, 0.0329 mol) was added to a mixture of PPh₃ (17 g, 0.065 mol) in dry benzene (60 mL), and the resulting mixture was stirred at room temperature for 30 min. 3,5-Bis(trifluoromethyl)benzophenone (4.0 g, 0.013 mol) was added in one portion, and the resulting mixture was heated to reflux for 48 h. The crude reaction product was filtered and washed with benzene (2 × 40 mL). Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂ 10:1 to 5:1) afforded **5e** (4.5 g, 73%) as an off-white solid. $R_f = 0.66$ (hexanes/CH₂Cl₂ 2:1); m.p. 51–52 °C; ¹H NMR (CDCl₃, 300 MHz): $\delta = 7.59$ –7.56 (m, 4H), 7.50–7.43 ppm (m, 4H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 144.9$, 141.3, 132.2, 131.2 (q, $J(C,F) = 33$ Hz), 129.2, 125.7 (q, $J(C,F) = 3.9$ Hz), 125.2 (q, $J(C,F) = 3.3$ Hz), 123.7 (q, $J(C,F) = 272$ Hz), 93.5 ppm; IR (CH₂Cl₂, cast): $\tilde{\nu} = 3071$, 3042 cm⁻¹; HRMS (EI): m/z calcd for C₁₆H₈F₆⁷⁹Br₂: 471.8897 [M^+]; found: 471.8887.

Compound 7: A mixture of trimer **6** (75 mg, 0.087 mmol) and TBAF (0.20 mL, 0.20 mmol, 1 M in THF) in wet THF (2 mL) was stirred for 1 h. Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. The resulting Et₂O solution was added to a degassed mixture of dibromoolefin **5e** (38 mg, 0.080 mmol), CuI (5.5 mg, 0.028 mmol), [Pd(PPh₃)₄] (4 mg, 0.003 mmol), *i*Pr₂NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂ 5:1 to 4:1) afforded **7** (56 mg, 68%) as a bright yellow solid. $R_f = 0.7$ (hexanes/CH₂Cl₂, 1:1); m.p. 244–245 °C; ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.60$ (d, $J = 7.6$ Hz, 2H), 7.42 (d, $J = 8$ Hz, 2H), 7.27–7.02 ppm (m, 34H); ¹⁹F NMR (376 MHz, CDCl₃) $\delta = -63.4$ ppm; ¹³C NMR (125 MHz, CD₂Cl₂): $\delta = 152.8$, 152.4, 147.4, 140.13, 140.07, 140.0, 139.7, 133.4, 130.6 (q, $J(C,F) = 32$ Hz) 130.3, 130.2, 129.4, 129.3, 129.22, 129.20, 128.4, 128.3, 128.2, 126.9 (q, $J(C,F) = 4$ Hz), 125.9 (q, $J(C,F) = 4$ Hz) 124.3 (q, $J(C,F) = 272$ Hz), 105.5, 102.4, 102.2, 98.8, 97.4, 96.7, 95.8 ppm (one signal coincident or not observed); IR (CH₂Cl₂, cast): $\tilde{\nu} = 3055$, 2925, 2170, 1684 cm⁻¹; UV/Vis (THF): $\lambda_{max}(\epsilon) = 430$ (sh; 21 000), 376 nm (81 800 M⁻¹ cm⁻¹); HRMS (MALDI-TOF; DCTB): m/z calcd for C₆₆H₃₈F₆: 944.28722 [M^+]; found: 944.28598.

Compound 8: A mixture of **6** (60 mg, 0.069 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M in THF) in wet THF (2 mL) was stirred for 1 h. Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. The resulting solution in Et₂O was added to a degassed mixture of dibromoolefin **5a** (24 mg, 0.071 mmol), CuI (6 mg, 0.03 mmol), [Pd(PPh₃)₄] (5 mg, 0.004 mmol), *i*Pr₂NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂ 5:1 to 2:1) afforded **8** (44 mg, 79%) as a bright yellow solid. $R_f = 0.7$ (hexanes/CH₂Cl₂, 1:1); m.p. >300 °C (decomp); ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.54$ –7.39 (m, 10H), 7.34–7.30 (m, 8H), 7.24–7.08 (m, 18H), 6.77–6.73 ppm (m, 2H); ¹³C NMR (125 MHz, CD₂Cl₂): $\delta = 153.4$, 152.6, 141.5, 140.9, 140.2, 139.6, 137.0, 130.4, 130.34, 130.27, 129.8, 129.52, 129.50, 129.3, 129.0, 128.4, 128.0, 124.9, 119.7, 104.3, 102.8, 102.5, 100.7, 97.4, 96.7 ppm (three signals coincident or not observed); IR (CH₂Cl₂, cast): $\tilde{\nu} = 3053$, 2921, 2849, 2153, 1941, 1880, 1814, 1600 cm⁻¹; UV/Vis (THF): $\lambda_{max}(\epsilon) = 470$ (sh; 15 000), 393 nm (86 500 M⁻¹ cm⁻¹); HRMS (MALDI-TOF; DCTB): m/z calcd for C₆₄H₃₈: 806.29680 [M^+]; found: 806.29551.

Compound 9: A mixture of trimer **6** (70 mg, 0.081 mmol) and TBAF (0.3 mL, 0.3 mmol, 1 M in THF) in wet THF (2 mL) was stirred for 1 h. Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. The resulting Et₂O solution was added to a degassed mixture of dibromoolefin **5d** (43 mg, 0.080 mmol), CuI (6.0 mg, 0.031 mmol), [Pd(PPh₃)₄] (6.5 mg, 0.0056 mmol), *i*Pr₂NH (3 mL), and dry THF (5 mL). The result-

ing mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂ 5:1 to 3:1) afforded radialene **9** (52 mg, 64%) as a brown solid. $R_f=0.7$ (hexanes/CH₂Cl₂, 1:1); m.p. >300 °C (decomp); ¹H NMR (CD₂Cl₂, 500 MHz): $\delta=7.35\text{--}6.96$ (m, 42H), 6.76–6.59 ppm (m, 8H); ¹³C NMR (125 MHz, CD₂Cl₂): $\delta=153.9, 151.6, 150.6, 145.3, 140.6, 140.1, 139.9, 135.7, 134.7, 133.3, 131.3, 131.0, 130.6, 130.5, 130.3, 129.6, 129.3, 129.0, 128.5, 128.3, 128.1, 127.5, 127.4, 126.9, 126.3, 113.5, 108.7, 102.5, 101.7, 98.1, 97.6, 95.5$ ppm; IR (CH₂Cl₂, cast): $\tilde{\nu}=3080, 3053, 3028, 2953, 2924, 2853, 2157, 2139, 1947, 1884, 1801, 1734$ cm⁻¹; UV/Vis (THF): $\lambda_{\text{max}}(\epsilon)=455$ (sh; 10000 M⁻¹cm⁻¹), 403 nm (20600); HRMS (MALDI-TOF; DCTB): m/z calcd for C₈₀H₅₀: 1010.39070 [M^+]; found: 1010.38941.

Crystal data for 9: C₈₀H₅₀; $M_r=1083.30$; crystal dimensions 0.57 × 0.20 × 0.18 mm; triclinic space group $P\bar{1}$; $a=13.6085(8)$, $b=14.1869(8)$, $c=16.5893(9)$ Å; $\alpha=90.6423(10)$, $\beta=104.8803(10)$, $\gamma=108.3368(9)^\circ$; $V=2923.4(3)$ Å³; $Z=2$; $\rho_{\text{calcd}}=1.231$ g cm⁻³; $\mu=0.071$ mm⁻¹; $\lambda=0.71073$ Å; $T=-80$ °C; $2\theta_{\text{max}}=52.00^\circ$, total data collected = 22506; $R_1(F)=0.0496$ (7164 observations [$F_o^2 \geq 2\sigma(F_o^2)$]); $wR_2(F^2)=0.1368$ for 721 variables and 11454 unique data; residual electron density = 0.200 and -0.139 e Å⁻³.

Compound 10: A mixture of timer **6** (90.0 mg, 0.104 mmol) and TBAF (0.3 mL, 0.3 mmol, 1 M in THF) in wet THF (2 mL) was stirred for 1 h. Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. The resulting solution in Et₂O was added to a degassed mixture of dibromoolefin **5b** (57.2 mg, 0.104 mmol), CuI (6 mg, 0.03 mmol), [Pd(PPh₃)₄] (6.5 mg, 0.0056 mmol), *i*Pr₂NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂ 5:1 to 2:1) afforded radialene **10** (82 mg, 77%) as a yellow solid. $R_f=0.62$ (hexanes/CH₂Cl₂, 1:1); m.p. 273 °C (decomp); ¹H NMR (CDCl₃, 500 MHz): $\delta=7.39\text{--}7.37$ (m, 4H), 7.27–7.13 (m, 22H), 7.06–7.03 (m, 4H), 0.89–0.83 ppm (m, 42H); ¹³C NMR (125 MHz, CDCl₃): $\delta=151.8, 151.6, 140.0, 139.9, 139.8, 130.5, 130.2, 130.1, 128.9, 128.7, 128.5, 127.9, 127.8, 127.7, 117.6, 110.9, 104.0, 103.8, 102.6, 102.1, 102.0, 96.6, 96.5, 96.3, 18.5, 11.1$ ppm; IR (CH₂Cl₂, cast): $\tilde{\nu}=3054, 2925, 2863, 2137$ cm⁻¹; UV/Vis (THF): $\lambda_{\text{max}}(\epsilon)=430$ (sh; 19100), 388 nm (47500 M⁻¹cm⁻¹); HRMS (MALDI-TOF; DCTB): m/z calcd for C₇₄H₇₂Si₂: 1016.51671 [M^+]; found: 1016.51720; DSC: decomposition, 271 °C (onset), 303 °C (peak).

Compound 12: A mixture of dimer **11** (53 mg, 0.080 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M in THF) in wet THF (2 mL) was stirred for 1 h. Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. The resulting Et₂O solution was added to a degassed mixture of dibromoolefin **5e** (38 mg, 0.080 mmol), CuI (5.0 mg, 0.025 mmol), [Pd(PPh₃)₄] (4.5 mg, 0.0039 mmol), *i*Pr₂NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂ 5:1 to 2:1) afforded **12** (5.9 mg, 10%) as a bright yellow solid. $R_f=0.65$ (hexanes/CH₂Cl₂, 1:1); m.p. 200 °C (decomp); ¹H NMR (C₂D₂Cl₄, 400 MHz): $\delta=8.00$ (s, 2H), 7.69–7.52 (m, 14H), 7.44–7.39 ppm (m, 12H); ¹⁹F NMR (376 MHz, C₂D₂Cl₄): $\delta=-63.1$ ppm; ¹³C NMR (125 MHz, CD₂Cl₂): $\delta=147.2, 142.3, 140.0, 139.7, 139.4, 133.9, 131.1, 130.8, 130.6, 129.7, 129.3, 128.5, 128.4, 127.2$ (q, $J(C,F)=4$ Hz), 126.2 (q, $J(C,F)=4$ Hz), 124.5 (q, $J(C,F)=273$ Hz), 110.2, 106.5, 94.3, 92.2, 91.1 ppm (one $J(C,F)$ quartet cannot be discerned due to low signal-to-noise (S/N) or coincident signals); IR (CH₂Cl₂, cast): $\tilde{\nu}=3058$ cm⁻¹; UV/Vis (THF): $\lambda_{\text{max}}(\epsilon)=412$ (18800), 363 nm (19200 M⁻¹cm⁻¹); HRMS (EI): m/z calcd for C₅₀H₂₈F₆: 742.20953 [M^+]; found: 742.21041.

Compound 13: A mixture of dimer **11** (65 mg, 0.099 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M in THF) in wet THF (2 mL) was stirred for 1 h. Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. The resulting solution in Et₂O was added to a degassed mixture of dibromoolefin **5a** (33 mg, 0.098 mmol), CuI (6 mg, 0.03 mmol), [Pd(PPh₃)₄] (6 mg, 0.005 mmol), *i*Pr₂NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 20 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂ 5:1) afforded **13** (26.8 mg, 45%) as a bright yellow solid. $R_f=0.6$ (hexanes/CH₂Cl₂, 1:1);

m.p. >300 °C (decomp); ¹H NMR (CD₂Cl₂, 400 MHz): $\delta=8.44$ (d, $J=7.6$ Hz, 2H), 7.73–7.65 (m, 10H), 7.55–7.53 (m, 6H), 7.46–7.43 (m, 6H), 7.39 (td, $J=6.8, 0.8$ Hz, 2H), 7.31 ppm (td, $J=6.8, 1.2$ Hz, 2H); ¹³C NMR (125 MHz, CD₂Cl₂): $\delta=147.5, 140.8, 139.8, 139.5, 137.4, 137.3, 130.9, 130.8, 130.1, 129.9, 129.8, 128.6, 128.4, 127.9, 124.9, 120.3, 107.0, 103.7, 99.9, 92.4, 90.6$ ppm; IR (CH₂Cl₂, cast): $\tilde{\nu}=3085, 3054, 3019, 2111, 1616, 1598, 1577, 1544$ cm⁻¹; UV/Vis (THF): $\lambda_{\text{max}}(\epsilon)=474$ (12000), 447 (14100), 383 nm (16100 M⁻¹cm⁻¹); HRMS (EI): m/z calcd for C₄₈H₂₈: 604.2191 [M^+]; found: 604.2191.

Compound 14: A mixture of **11** (85 mg, 0.13 mmol) and TBAF (0.3 mL, 0.3 mmol, 1 M in THF) in wet THF (2 mL) was stirred for 1 h. Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. The resulting Et₂O solution was added to a degassed mixture of dibromoolefin **5c** (50.2 mg, 0.130 mmol), CuI (7.5 mg, 0.040 mmol), [Pd(PPh₃)₄] (7.5 mg, 0.0060 mmol), *i*Pr₂NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 20 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂ 5:1) afforded compound **14** (34 mg, 40%) as an orange solid. $R_f=0.45$ (hexanes/CH₂Cl₂, 1:1); m.p. 220 °C; ¹H NMR (CD₂Cl₂, 400 MHz): $\delta=7.65\text{--}7.63$ (m, 8H), 7.53–7.40 ppm (m, 22H); ¹³C NMR (125 MHz, CD₂Cl₂): $\delta=147.8, 139.8, 139.5, 132.3, 131.0, 130.8, 129.9, 129.73, 129.68, 128.9, 128.6, 128.4, 123.8, 122.6, 106.8, 106.6, 100.1, 99.2, 92.2, 91.8, 87.2$ ppm; IR (CH₂Cl₂, cast): $\tilde{\nu}=3079, 3057, 3032, 3019, 2208, 2188, 2109, 1596$ cm⁻¹; UV/Vis (THF): $\lambda_{\text{max}}(\epsilon)=482$ (27000), 457 (29400), 388 nm (35100 M⁻¹cm⁻¹); HRMS (MALDI-TOF; DCTB): m/z calcd for C₅₂H₃₀: 654.23420 [M^+]; found: 654.23448.

Crystal data for 14: C₅₂H₃₀; $M_r=654.76$; crystal dimensions 0.31 × 0.29 × 0.16 mm; triclinic space group $P\bar{1}$; $a=10.1840(3)$, $b=13.3163(4)$, $c=14.8691(5)$ Å; $\alpha=115.0722(4)$, $\beta=92.1370(4)$, $\gamma=94.4601(4)^\circ$; $V=1815.40(10)$ Å³; $Z=2$; $\rho_{\text{calcd}}=1.198$ g cm⁻³; $\mu=0.068$ mm⁻¹; $\lambda=0.71073$ Å; $T=-100$ °C; $2\theta_{\text{max}}=51.48^\circ$, total data collected = 13653; $R_1(F)=0.0438$ (5517 observations [$F_o^2 \geq 2\sigma(F_o^2)$]); $wR_2(F^2)=0.1242$ for 469 variables and 6920 unique data; residual electron density = 0.732 and -0.189 e Å⁻³.

Compound 15: A mixture of **11** (60 mg, 0.091 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M in THF) in wet THF (2 mL) was stirred for 1 h. Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. The resulting solution in Et₂O was added to a degassed mixture of dibromoolefin **5b** (50 mg, 0.091 mmol), CuI (6.0 mg, 0.030 mmol), [Pd(PPh₃)₄] (5.0 mg, 0.0040 mmol), *i*Pr₂NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂ 5:1 to 2:1) afforded **15** (24.6 mg, 33%) as a yellow solid. $R_f=0.75$ (hexanes/CH₂Cl₂, 1:1); m.p. 195 °C (decomp); ¹H NMR (CD₂Cl₂, 400 MHz): $\delta=7.59\text{--}7.53$ (m, 8H), 4.71–7.39 (m, 12H), 1.10–1.08 ppm (m, 42H); ¹³C NMR (125 MHz, CD₂Cl₂): $\delta=147.7, 139.7, 139.5, 130.8, 130.7, 129.7, 129.6, 128.6, 128.4, 123.5, 107.2, 106.5, 103.7, 102.7, 99.9, 92.0, 91.6, 18.8, 11.6$ ppm; IR (CH₂Cl₂, cast): $\tilde{\nu}=3058, 2995, 2941, 2925, 2864, 2100, 1737$ cm⁻¹; UV/Vis (THF): $\lambda_{\text{max}}(\epsilon)=450$ (sh; 23300), 430 (31800), 378 nm (42800 M⁻¹cm⁻¹); HRMS (MALDI-TOF; DCTB): m/z calcd for C₅₈H₆₂Si₂: 814.43846 [M^+]; found: 814.43868.

Compound 16: Trimethylsilylacetylene (330 mg, 3.4 mmol, 0.48 mL) was added to a degassed mixture of **5e** (79 mg, 0.17 mmol), CuI (3.2 mg, 0.016 mmol), [Pd(PPh₃)₂Cl₂] (5.8 mg, 0.0082 mmol), *i*Pr₂NH (3 mL), and dry THF (10 mL). The resulting mixture was heated to reflux for 18 h. Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), and dried (MgSO₄). Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂ 10:1) afforded **16** (76 mg, 88%) as a white solid. $R_f=0.7$ (hexanes/CH₂Cl₂, 2:1); m.p. 120 °C; ¹H NMR (CDCl₃, 500 MHz): $\delta=7.84$ (s, 2H), 7.58–7.57 (m, 2H), 7.42–7.41 (m, 4H), 0.08 ppm (s, 18H); ¹³C NMR (125 MHz, CDCl₃): $\delta=153.7, 140.1, 133.4, 130.3$ (q, $J(C,F)=32.3$ Hz), 128.4, 127.0 (q, $J(C,F)=3.8$ Hz), 125.3 (q, $J(C,F)=3.8$ Hz), 124.0 (q, $J(C,F)=271$ Hz), 104.7, 101.8, 99.9, -0.65 ppm; IR (CH₂Cl₂, cast): $\tilde{\nu}=3071, 2961, 2901, 2150, 2132$ cm⁻¹; HRMS (EI): m/z calcd for C₂₆H₂₆F₆Si₂: 508.1477 [M^+]; found: 508.1490.

Compound 18: A mixture of **16** (55 mg, 0.11 mmol) and K_2CO_3 (2.9 mg, 0.020 mmol) in wet THF (1 mL) and MeOH (1 mL) was stirred for 1 h. Et_2O and H_2O were added; the organic phase was separated, washed with saturated NH_4Cl (2×20 mL), dried ($MgSO_4$), and reduced to 2 mL. The resulting solution in Et_2O was added to a degassed mixture of triflate **17** (101 mg, 0.206 mmol), CuI (6.4 mg, 0.33 mmol), $[Pd(PPh_3)_4]$ (7 mg, 0.006 mmol), iPr_2NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/ CH_2Cl_2 1:10–5:1) afforded **18** (81 mg, 74%) as a bright yellow solid. $R_f=0.5$ (hexanes/ CH_2Cl_2 2:1); m.p. 85°C; 1H NMR ($CDCl_3$, 400 MHz): $\delta=7.57$ – 7.55 (m, 2H), 7.50–7.40 (m, 2H), 7.39–7.19 (m, 24H), 0.79 (s, 18H), 0.01 ppm (s, 12H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=157.8$, 150.8, 140.2, 140.0, 139.6, 133.5, 130.5, 130.3, 130.2, 128.7, 128.5, 128.3, 127.7, 127.6, 126.9 (q, $J(C,F)=4$ Hz), 125.4 ($J(C,F)=3.2$ Hz), 123.9 (q, $J(C,F)=273$ Hz), 104.8, 103.1, 101.5, 96.3, 92.2, 88.6, 26.1, 16.7, -4.9 ppm (one $J(C,F)$ quartet cannot be discerned due to low S/N or coincident signals); IR (CH_2Cl_2 , cast): $\tilde{\nu}=3056$, 2954, 2928, 2856, 2192, 2097, 2143 cm^{-1} ; UV/Vis (THF): $\lambda_{max}=304$, 366 nm; HRMS (MALDI-TOF; DCTB): m/z calcd for $C_{64}H_{38}F_6Si_2$: 996.39758 [M^+]; found: 996.39787.

Compound 19: A mixture of trimer **18** (32 mg, 0.032 mmol) and TBAF (0.03 mL, 0.03 mmol, 1 M in THF) in wet THF (2 mL) was stirred for 1 h. Et_2O and H_2O were added; the organic phase was separated, washed with saturated NH_4Cl (2×20 mL), dried ($MgSO_4$), and reduced to 2 mL. The resulting solution in Et_2O was added to a degassed mixture of dibromoolefin **5e** (15 mg, 0.032 mmol), CuI (1 mg, 0.005 mmol), $[Pd(PPh_3)_4]$ (1.8 mg, 0.0015 mmol), iPr_2NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/ CH_2Cl_2 5:1 to 3:1) afforded **19** (22 mg, 64%) as a bright yellow solid. $R_f=0.63$ (hexanes/ CH_2Cl_2 , 1.5:1); m.p. $>205^\circ C$ (decomp); 1H NMR (CD_2Cl_2 , 500 MHz): $\delta=7.66$ (d, $J=8$ Hz, 4H), 7.51 (d, $J=8$ Hz, 4H), 7.25–7.19 (m, 20H), 7.09–7.07 ppm (m, 8H); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta=-63.4$ ppm; ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta=153.8$, 147.9, 140.1, 139.7, 133.5, 130.7 (q, $J(C,F)=32.4$ Hz) 130.3, 129.5, 129.3, 128.2, 127.0 (q, $J(C,F)=4$ Hz), 126.1 (q, $J(C,F)=3.8$ Hz) 124.3 (q, $J(C,F)=272$ Hz) 105.40, 101.8, 98.4, 96.1 ppm; IR (CH_2Cl_2 , cast): $\tilde{\nu}=3081$, 3056, 3030, 2151 cm^{-1} ; UV/Vis (THF): $\lambda_{max}(\epsilon)=430$ (sh; 35000), 376 nm ($122000 M^{-1}cm^{-1}$); HRMS (MALDI-TOF; DCTB): m/z calcd for $C_{68}H_{36}F_{12}$: 1080.26199 [M^+]; found: 1080.26221.

Crystal data for 19: $C_{68}H_{36}F_{12}$, $M_r=1080.97$; crystal dimensions 0.26 \times 0.16 \times 0.14 mm; triclinic space group $P\bar{1}$; $a=5.8220(6)$, $b=14.8570(17)$, $c=15.6024(17)$ Å; $\alpha=108.0127(17)$, $\beta=92.5579(18)$, $\gamma=90.3119(19)^\circ$; $V=1281.9(2)$ Å³; $Z=1$; $\rho_{calcd}=1.400$ g cm^{-3} ; $\mu=0.111$ mm⁻¹; $\lambda=0.71073$ Å; $T=-80^\circ C$; $2\theta_{max}=52.76^\circ$, total data collected=10260; $R_1(F)=0.0460$ (3746 observations [$F_o \geq 2\sigma(F_o)$]); $wR_2(F^2)=0.1348$ for 361 variables and 5223 unique data; residual electron density=0.368 and -0.290 e Å⁻³.

Compound 22: A mixture of **20** (150 mg, 0.361 mmol) and K_2CO_3 (10 mg, 0.07 mmol) in wet THF (1 mL) and MeOH (1 mL) was stirred for 2 h. Et_2O and H_2O were added; the organic phase was separated, washed with saturated NH_4Cl (2×20 mL), dried ($MgSO_4$), and reduced to 2 mL. The solution of **21** in Et_2O was added to a degassed mixture of dibromoolefin **5b** (98 mg, 0.18 mmol), CuI (21 mg, 0.11 mmol), $[Pd(PPh_3)_4]$ (20.8 mg, 0.0179 mmol), iPr_2NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/ CH_2Cl_2 10:1 to 5:1) afforded **22** (95 mg, 49%) as a yellow oil (solidified when stored at 4°C). $R_f=0.3$ (hexanes/ CH_2Cl_2 5:1); 1H NMR (300 MHz, $CDCl_3$): $\delta=7.39$ – 7.35 (m, 8H), 7.30–7.28 (m, 6H), 7.25–7.23 (m, 6H), 1.09–1.05 (m, 42H), 0.87 (t, $J=7.8$ Hz, 18H), 0.50 ppm (q, $J=7.8$ Hz, 12H); ^{13}C NMR (125 Hz, $CDCl_3$): $\delta=158.0$, 140.6, 139.6, 130.33, 130.29, 128.7, 128.3, 127.7, 127.6, 118.1, 116.5, 103.7, 103.6, 101.79, 101.77, 97.3, 95.6, 88.3, 18.6, 11.2, 7.3, 4.2 ppm; IR (CH_2Cl_2 , cast): $\tilde{\nu}=3082$, 3056, 2956, 2890, 2866, 2182, 2143 cm^{-1} ; HRMS (MALDI-TOF; DCTB): m/z calcd for $C_{72}H_{92}Si_4$: 1068.62706 [M^+]; found: 1068.62743.

Compound 23: A mixture of **22** (45 mg, 0.042 mmol) and K_2CO_3 (8.1 mg, 0.21 mmol) in wet THF (1 mL) and MeOH (2 mL) was stirred for 2 h. Et_2O and H_2O were added; the organic phase was separated, washed

with saturated NH_4Cl (2×20 mL), dried ($MgSO_4$), and reduced to 2 mL. The resulting solution in Et_2O was added to a degassed mixture of dibromoolefin **5b** (23 mg, 0.042 mmol), CuI (6.0 mg, 0.031 mmol), $[Pd(PPh_3)_4]$ (4.4 mg, 0.0038 mmol), iPr_2NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/ CH_2Cl_2 5:1 to 2:1) afforded **23** (40 mg, 78%) as a yellow solid. $R_f=0.6$ (hexanes/ CH_2Cl_2 , 1:1); m.p. 235°C; 1H NMR ($CDCl_3$, 400 MHz): $\delta=7.38$ – 7.36 (m, 8H), 7.26–7.23 (m, 12H), 0.95–0.93 ppm (m, 84H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=153.0$, 139.9, 130.7, 129.1, 127.7, 117.0, 111.5, 104.1, 103.9, 102.3, 101.8, 95.8, 18.6, 11.2 ppm; IR (CH_2Cl_2 , cast): $\tilde{\nu}=2941$, 2924, 2890, 2863, 2165, 2134 cm^{-1} ; UV/Vis (THF): $\lambda_{max}(\epsilon)=430$ (sh; 16000), 399 nm (sh; 25500 $M^{-1}cm^{-1}$); HRMS (MALDI-TOF; DCTB): m/z calcd for $C_{84}H_{104}Si_4$: 1224.72096 [M^+]; found: 1224.72033.

Crystal data for 23: $C_{84}H_{104}Si_4$, $M_r=1226.03$; crystal dimensions 0.52 \times 0.27 \times 0.11 mm; monoclinic space group $P2_1/c$ (no. 14); $a=21.031(3)$, $b=13.0172(17)$, $c=15.048(2)$ Å; $\beta=106.788(2)^\circ$; $V=3943.9(9)$ Å³; $Z=2$; $\rho_{calcd}=1.032$ g cm^{-3} ; $\mu=0.115$ mm⁻¹; $\lambda=0.71073$ Å; $T=-80^\circ C$; $2\theta_{max}=50.00^\circ$, total data collected=26078; $R_1(F)=0.0648$ (4989 observations [$F_o \geq 2\sigma(F_o)$]); $wR_2(F^2)=0.1955$ for 397 variables and 6944 unique data; residual electron density=0.389 and -0.205 e Å⁻³.

Compound 24: TBAF (0.1 mL, 0.1 mmol, 1.0 M in THF) was added to a solution of radialene **10** (25 mg, 0.025 mmol) in wet THF (10 mL) at 0°C, and the solution was stirred until the starting material was no longer visible by TLC analysis (≈ 5 –10 min). Et_2O and H_2O were added; the organic phase was separated, washed with saturated NH_4Cl (2×20 mL), dried ($MgSO_4$), and reduced to 2 mL. This Et_2O solution was then added to a degassed solution of 4-iodobenzonitrile (11 mg, 0.050 mmol) in THF (3 mL). iPr_2NH (2 mL), $[Pd(PPh_3)_4]$ (1.4 mg, 0.0012 mmol), and CuI (0.6 mg, 0.003 mmol) were added sequentially to this solution, and the solution was stirred at approximately 50°C under N_2 until TLC analysis no longer showed the presence of the deprotected radialene (≈ 15 –18 h). Aqueous workup, solvent removal, flash column chromatography (silica gel, CH_2Cl_2), and precipitation from CH_2Cl_2 by the addition of Et_2O afforded **24** as an orange solid (17 mg, 75%). $R_f=0.49$ (CH_2Cl_2); m.p. 286–288°C (discolors, decomp); DSC: decomposition, 304°C (onset), 319°C (peak). 1H NMR (500 MHz, CD_2Cl_2): $\delta=7.56$ (d, $J=8.6$ Hz, 4H), 7.45–7.43 (m, 4H), 7.31–7.18 (m, 28H), 7.02–6.99 ppm (m, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta=154.0$, 153.1, 140.12, 140.07, 139.7, 132.7, 132.3, 131.0, 130.4, 130.3, 129.7, 129.6, 129.3, 128.41, 128.39, 128.3, 127.0, 120.4, 118.7, 112.6, 108.9, 106.6, 102.2, 102.0, 97.3, 96.6, 96.4, 96.2, 90.1 ppm; IR (CH_2Cl_2 , cast): $\tilde{\nu}=3062$, 2225, 2157, 1602 cm^{-1} ; UV/Vis (CH_2Cl_2): $\lambda_{max}(\epsilon)=498$ (sh; 13200), 401 (76800), 339 (52300), 261 nm ($48000 M^{-1}cm^{-1}$); HRMS (MALDI-TOF; DCTB): m/z calcd for $C_{70}H_{38}N_2$: 906.3030 [M^+]; found: 906.3026.

Compound 25: TBAF (0.1 mL, 0.1 mmol, 1.0 M in THF) was added to a solution of radialene **10** (27 mg, 0.027 mmol) in wet THF (10 mL) at 0°C, and the solution was stirred until the starting material was no longer visible by TLC analysis (≈ 5 –10 min). Et_2O and H_2O were added; the organic phase was separated, washed with saturated NH_4Cl (2×20 mL), dried ($MgSO_4$), and reduced to 2 mL. This solution in Et_2O was then added to a degassed solution of 4-iodonitrobenzene (13 mg, 0.054 mmol) in THF (10 mL). iPr_2NH (2 mL), $[Pd(PPh_3)_4]$ (1.6 mg, 0.0014 mmol), and CuI (1 mg, 0.003 mmol) were added sequentially to this solution, and the solution was stirred at approximately 50°C under N_2 until TLC analysis no longer showed the presence of the deprotected radialene (≈ 15 –18 h). Aqueous workup, solvent removal, and flash column chromatography (silica gel, CH_2Cl_2) followed by precipitation from CH_2Cl_2 by the addition of Et_2O afforded **25** (24 mg, 94%) as an orange solid. $R_f=0.66$ (CH_2Cl_2 /hexanes, 7:3); m.p. 285°C (discolors, decomp); DSC: decomposition, 297°C (onset), 306°C (peak); 1H NMR (500 MHz, CD_2Cl_2): $\delta=8.11$ (d, $J=9.0$ Hz, 4H), 7.47–7.45 (m, 4H), 7.31–7.13 (m, 28H), 7.03–7.00 ppm (m, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta=154.2$, 153.2, 147.8, 140.15, 140.06, 139.7, 133.1, 131.0, 130.4, 130.3, 129.72, 129.70, 129.3, 129.0, 128.42, 128.40, 128.3, 123.8, 120.9, 108.6, 107.0, 102.2, 101.9, 97.4, 96.39, 96.38, 96.2, 90.9 ppm; IR (CH_2Cl_2 , cast): $\tilde{\nu}=3099$, 2924, 2853, 2167, 1342 cm^{-1} ; UV/Vis (CH_2Cl_2): $\lambda_{max}(\epsilon)=497$ (sh; 13700), 402 (66800),

264 nm (38300 M⁻¹ cm⁻¹); HRMS (MALDI-TOF; DCTB): *m/z* calcd for C₆₈H₃₈N₂O₄: 946.2826 [M⁺]; found: 946.2821.

Compound 26: TBAF (0.1 mL, 0.1 mmol, 1.0 M in THF) was added to a solution of radialene **10** (25 mg, 0.025 mmol) in wet THF (10 mL) at 0 °C, and the solution was stirred until the starting material was no longer visible by TLC analysis (≈ 5–10 min). Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. This Et₂O solution was then added to a degassed solution of 4-iodo-*N,N*-diisopropylaniline (15 mg, 0.050 mmol) in THF (10 mL), *i*Pr₂NH (2 mL), [Pd(PPh₃)₄] (1.4 mg, 0.0012 mmol), and CuI (1 mg, 0.003 mmol) were added sequentially, and the solution was stirred at approximately 50 °C under N₂ until TLC analysis no longer showed the presence of the deprotected radialene (≈ 15–18 h). Aqueous workup, solvent removal, and flash column chromatography (silica gel, EtOAc/hexanes 1:10 to 3:10) followed by precipitation from CH₂Cl₂ by the addition of Et₂O afforded **26** (23 mg, 87%) as a red solid. *R*_f = 0.31 (EtOAc/hexanes 1:4); m.p. 281 °C (discolors, decomp); DSC: decomposition, 273 °C (onset), 285 °C (peak); ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.49–7.47 (m, 4H), 7.29–7.20 (m, 16H), 7.17–7.11 (m, 10H), 6.91 (d, *J* = 9.1 Hz, 4H), 6.68 (d, *J* = 9.1 Hz, 4H), 3.92 (sept, *J* = 6.9 Hz, 4H), 1.31 ppm (d, *J* = 6.9 Hz, 24H); ¹³C NMR (125 MHz, CD₂Cl₂): δ = 152.2, 151.8, 149.3, 140.3, 140.23, 140.19, 133.2, 130.9, 130.4, 130.3, 129.3, 129.14, 129.07, 128.30, 128.29, 128.25, 115.6, 113.4, 112.6, 108.6, 103.0, 102.6, 102.5, 101.3, 97.7, 97.0, 96.9, 86.7, 47.8, 21.2 ppm; IR (CH₂Cl₂, cast): $\tilde{\nu}$ = 3082, 3053, 2969, 2928, 2170, 1603, 1295 cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 542 (32400), 495 (31700), 401 (71100), 280 nm (47400 M⁻¹ cm⁻¹); HRMS (MALDI-TOF; DCTB): *m/z* calcd for C₈₀H₆₆N₂: 1054.5221 [M⁺]; found: 1054.5222.

CCDC-942885 (**5d**), -942886 (**9**), -942887 (**14**), -942888 (**19**), and -942889 (**23**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors are grateful for funding from NSERC, the University of Erlangen-Nuremberg, the Deutsche Forschungsgemeinschaft (DFG SFB 953, “Synthetic Carbon Allotropes”), the Interdisciplinary Center for Molecular Materials (ICMM), and the “Excellence Initiative” supporting the Cluster of Excellence “Engineering of Advanced Materials”. L.E. thanks the US NSF for generous financial support (grant nos. DMR-1205302 and CHE-1124075) and the Robert A. Welch Foundation for an endowed chair (grant no. AH-0033). M.N.C. thanks the Centro de Excelencia en Nuevos Materiales (CENM) and the Vicerrectoría de Investigaciones of Universidad del Valle.

- [1] T. S. Perry, *Spectrum, IEEE Spectrum* **2013**, *50*, 46–47.
- [2] S. Bae, H. Kim, Y. Lee, X. F. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong, S. Iijima, *Nat. Nanotechnol.* **2010**, *5*, 574–578.
- [3] T. Liu, A. Troisi, *Adv. Mater.* **2013**, *25*, 1038–1041.
- [4] For reviews, see: a) M. Iyoda, J. Yamakawa, M. J. Rahman, *Angew. Chem.* **2011**, *123*, 10708–10740; *Angew. Chem. Int. Ed.* **2011**, *50*, 10522–10553; b) *Modern Supramolecular Chemistry: Strategies in Macrocyclic Synthesis* (Eds.: F. Diederich, P. J. Stang, R. Tykwinski), Wiley-VCH, Weinheim, **2008**; c) K. Tahara, Y. Tobe, *Chem. Rev.* **2006**, *106*, 5274–5290; d) *Carbon-Rich Compounds: Molecules to Materials* (Eds.: M. M. Haley, R. R. Tykwinski), Wiley-VCH, Weinheim, **2006**; e) U. H. F. Bunz, Y. Rubin, Y. Tobe, *Chem. Soc. Rev.* **1999**, *28*, 107–119.
- [5] E. L. Spittler, C. A. Johnson II, M. M. Haley, *Chem. Rev.* **2006**, *106*, 5344–5386.
- [6] a) S. Rondeau-Gagne, J. R. Neabo, M. Desroches, J. Larouche, J. Brisson, J. F. Morin, *J. Am. Chem. Soc.* **2013**, *135*, 110–113; b) Y.

- Tobe, *J. Synth. Org. Chem. Jpn.* **2012**, *70*, 1255–1266; c) K. Campbell, K. J. Ooms, M. J. Ferguson, P. J. Stang, R. E. Wasylshen, R. R. Tykwinski, *Can. J. Chem.* **2011**, *89*, 1264–1276; d) D. Bonifazi, S. Mohnani, A. Llanes-Pallas, *Chem. Eur. J.* **2009**, *15*, 7004–7025; e) K. Campbell, C. J. Kuehl, M. J. Ferguson, P. J. Stang, R. R. Tykwinski, *J. Am. Chem. Soc.* **2002**, *124*, 7266–7267.
- [7] a) H. Miyake, T. Sasamori, N. Tokitoh, *Angew. Chem.* **2012**, *124*, 3514–3517; *Angew. Chem. Int. Ed.* **2012**, *51*, 3458–3461; b) V. Maraval, R. Chauvin, *Chem. Rev.* **2006**, *106*, 5317–5343; c) F. Geneste, A. Moradpour, *Org. Prep. Proced.* **1999**, *31*, 509–536; d) T. Lange, V. Gramlich, W. Amrein, F. Diederich, M. Gross, C. Boudon, J.-P. Gisselbrecht, *Angew. Chem.* **1995**, *107*, 898–901; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 805–809; e) H. Hopf, G. Maas in *The Chemistry of Dienes and Polyenes, Vol. 1* (Ed.: Z. Rappoport), Wiley, Chichester, **1997**, pp. 927–977; f) H. Hopf, G. Maas, *Angew. Chem.* **1992**, *104*, 953–977; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 931–954.
- [8] a) F. Diederich, M. Kivala, *Adv. Mater.* **2010**, *22*, 803–812; b) M. Kivala, F. Diederich, *Acc. Chem. Res.* **2009**, *42*, 235–248; c) R. R. Tykwinski, M. Gholami, S. Eisler, Y. Zhao, F. Melin, L. Echegoyen, *Pure Appl. Chem.* **2008**, *80*, 621–637; d) M. Gholami, R. R. Tykwinski, *Chem. Rev.* **2006**, *106*, 4997–5027.
- [9] M. Kivala, F. Mitzel, C. Boudon, J. P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Asian J.* **2006**, *1*, 479–489.
- [10] a) M. Hasegawa, Y. Takatsuka, Y. Kuwatani, Y. Mazaki, *Tetrahedron Lett.* **2012**, *53*, 5385–5388; b) K. Lincke, A. F. Frellsen, C. R. Parker, A. D. Bond, O. Hammerich, M. B. Nielsen, *Angew. Chem. Int. Ed.* **2012**, *51*, 6099–6102; c) Y.-L. Wu, F. Bures, P. D. Jarowski, W. B. Schweizer, C. Boudon, J. P. Gisselbrecht, F. Diederich, *Chem. Eur. J.* **2010**, *16*, 9592–9605; d) M. Gholami, M. N. Chaur, M. Wilde, M. J. Ferguson, R. McDonald, L. Echegoyen, R. R. Tykwinski, *Chem. Commun.* **2009**, 3038–3040; e) G. Chen, L. Dawe, L. Wang, Y. Zhao, *Org. Lett.* **2009**, *11*, 2736–2739; f) A. Bandyopadhyay, B. Varghese, H. Hopf, S. Sankararaman, *Chem. Eur. J.* **2007**, *13*, 3813–3821; g) F. Mitzel, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Helv. Chim. Acta* **2004**, *87*, 1130–1157; h) F. Mitzel, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Commun.* **2003**, 1634–1635.
- [11] a) B. J. Coe, J. Fielden, S. P. Foxon, M. Helliwell, I. Asselberghs, K. Clays, K. De Mey, B. S. Brunshwig, *J. Org. Chem.* **2010**, *75*, 8550–8563; b) E. Opsitnick, D. Lee, *Chem. Eur. J.* **2007**, *13*, 7040–7049; c) U. Gubler, R. Spreiter, C. Bosshard, P. Gunter, R. R. Tykwinski, F. Diederich, *Appl. Phys. Lett.* **1998**, *73*, 2396–2398.
- [12] P. A. Limacher, H. P. Luthi, *WIREs Comput. Mol. Sci.* **2011**, *1*, 477–486.
- [13] a) N. F. Phelan, M. Orchin, *J. Chem. Educ.* **1968**, *45*, 633–637; b) M. Trætteberg, H. Hopf, *Acta Chem. Scand.* **1994**, *48*, 989–993.
- [14] a) F. Diederich, *Chem. Commun.* **2001**, 219–227; b) F. Diederich, *Chimia* **2001**, *55*, 821–827; c) F. Diederich, *Nature* **1994**, *369*, 199–207; d) F. Diederich, *Pure Appl. Chem.* **1999**, *71*, 265–273; e) F. Diederich, L. Gobbi, *Top. Curr. Chem.* **1999**, *201*, 43–79.
- [15] a) M. B. Nielsen, M. Schreiber, Y. G. Baek, P. Seiler, S. Lecomte, C. Boudon, R. R. Tykwinski, J. P. Gisselbrecht, V. Gramlich, P. J. Skinner, C. Bosshard, P. Günter, M. Gross, F. Diederich, *Chem. Eur. J.* **2001**, *7*, 3263–3280; b) A. M. Boldi, F. Diederich, *Angew. Chem.* **1994**, *106*, 482–485; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 468–471.
- [16] See also: a) Y.-L. Zhao, Q. Liu, J.-P. Zhang, Z.-Q. Liu, *J. Org. Chem.* **2005**, *70*, 6913–6917; b) Y. Tobe, R. Umeda, N. Iwasa, M. Sonoda, *Chem. Eur. J.* **2003**, *9*, 5549–5559.
- [17] M. Gholami, F. Melin, R. McDonald, M. J. Ferguson, L. Echegoyen, R. R. Tykwinski, *Angew. Chem.* **2007**, *119*, 9239–9243; *Angew. Chem. Int. Ed.* **2007**, *46*, 9081–9085.
- [18] S. Eisler, R. R. Tykwinski, *Angew. Chem.* **1999**, *111*, 2138–2141; *Angew. Chem. Int. Ed.* **1999**, *38*, 1940–1943.
- [19] So-called “hybrid” expanded radialenes have been reported in which the symmetrical enyne framework of **2** and **3** is altered with other π spacers. See, for example: a) M. Iyoda, Y. Kuwatani, S. Yamagata, N. Nakamura, M. Todaka, G. Yamamoto, *Org. Lett.* **2004**, *6*, 4667–4670; b) K. Campbell, N. M. Tiemstra, N. S. Prepas-Strobeck, R. McDonald, M. J. Ferguson, R. R. Tykwinski, *Synlett* **2004**, 182–

- 186; c) K. Campbell, C. A. Johnson II, R. McDonald, M. J. Ferguson, M. M. Haley, R. R. Tykwinski, *Angew. Chem.* **2004**, *116*, 6093–6097; *Angew. Chem. Int. Ed.* **2004**, *43*, 5967–5971; d) R. Faust, F. Diederich, V. Gramlich, P. Seiler, *Chem. Eur. J.* **1995**, *1*, 111–117; e) R. Gleiter, H. Röckel, B. Nuber, *Tetrahedron Lett.* **1994**, *35*, 8779–8782; f) R. Gleiter, H. Röckel, H. Irngartinger, T. Oeser, *Angew. Chem.* **1994**, *106*, 1340–1342; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1270–1272; see also ref. [6].
- [20] Y. Zhao, K. Campbell, R. R. Tykwinski, *J. Org. Chem.* **2002**, *67*, 336–344.
- [21] R. R. Tykwinski, Y. Zhao, *Synlett* **2002**, 1939–1953.
- [22] Y. Zhao, R. R. Tykwinski, *J. Am. Chem. Soc.* **1999**, *121*, 458–459.
- [23] Y. Zhao, A. D. Slepko, C. O. Akoto, R. McDonald, F. A. Hegmann, R. R. Tykwinski, *Chem. Eur. J.* **2005**, *11*, 321–329.
- [24] F. Ramirez, N. B. Desai, N. McKelvie, *J. Am. Chem. Soc.* **1962**, *84*, 1745–1747.
- [25] For synthesis of **5a**, see: G. C. Paul, J. J. Gajewski, *Synthesis* **1997**, 524–526.
- [26] For synthesis of **5b**, see: J. Anthony, A. M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C. B. Knobler, P. Seiler, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 13–45.
- [27] For synthesis of **5c**, see: R. R. Tykwinski, T. Luu, *Synthesis* **2012**, *44*, 1915–1922; D. Philp, V. Gramlich, P. Seiler, F. Diederich, *J. Chem. Soc. Perkin Trans. 2* **1995**, 875–886.
- [28] THF was used as a cosolvent to increase solubility of the precursors and reproducibility of the coupling reactions, as has been previously reported. See, for examples: a) S. Thorand, N. Krause, *J. Org. Chem.* **1998**, *63*, 8551–8553; b) Y. Tobe, K. Kubota, K. Naemura, *J. Org. Chem.* **1997**, *62*, 3430–3431; c) R. R. Tykwinski, F. Diederich, F. Gramlich, P. Seiler, *Helv. Chim. Acta* **1996**, *79*, 634–645.
- [29] For reviews of the Sonogashira reaction: a) R. Chinchilla, C. Najera, *Chem. Rev.* **2007**, *107*, 874–922; b) R. R. Tykwinski, *Angew. Chem.* **2003**, *115*, 1604–1606; *Angew. Chem. Int. Ed.* **2003**, *42*, 1566–1588; c) K. Sonogashira, *J. Organomet. Chem.* **2002**, *653*, 46–49.
- [30] See, for example, the following reports, as well as references cited therein: a) S. K. Collins, G. P. A. Yap, A. G. Fallis, *Org. Lett.* **2002**, *4*, 11–14; b) S. Eisler, R. McDonald, G. R. Lopponow, R. R. Tykwinski, *J. Am. Chem. Soc.* **2000**, *122*, 6917–6928.
- [31] Calculated from planes generated from the nine carbon atoms of the radialene and the six carbon atoms from the phenyl ring.
- [32] The plane consisted of the twelve carbon atoms of the radialene ring and alkylidene carbon atoms C3/C3'.
- [33] For example, see: A. Bhaskar, G. Ramakrishna, K. Hagedorn, O. Varnavski, E. Mena-Osteritz, P. Bäuerle, T. Goodson III, *J. Phys. Chem. B* **2007**, *111*, 946–954.
- [34] J. Anthony, A. M. Boldi, C. Boudon, J.-P. Gisselbrecht, M. Gross, P. Seiler, C. B. Knobler, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 797–817.
- [35] M. Iyoda, H. Kurata, M. Oda, C. Okubo, K. Nishimoto, *Angew. Chem.* **1993**, *105*, 97–99; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 89–90.
- [36] For example, see: a) B. B. Frank, M. Kivala, B. Camafort Blanco, B. Breiten, W. B. Schweizer, P. R. Laporta, I. Biaggio, E. Jahnke, R. R. Tykwinski, C. Boudon, J.-P. Gisselbrecht, F. Diederich, *Eur. J. Org. Chem.* **2010**, 2487–2503; b) J.-P. Gisselbrecht, N. N. P. Moonen, C. Boudon, M. B. Nielsen, F. Diederich, M. Gross, *Eur. J. Org. Chem.* **2004**, 2959–2972.

Received: June 25, 2013
Published online: September 20, 2013