Donor-Substituted Perethynylated Dehydroannulenes and Radiaannulenes: Acetylenic Carbon Sheets Featuring Intense Intramolecular Charge Transfer

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In this article, we report the preparation of unprecedented π-conjugated macrocycles (*Fig. 1*) by acetylenic scaffolding using modular tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne) building blocks. A novel photochemical access to (*Z*)-bisdeprotected TEEs (*Scheme 1*) enabled the synthesis of the anilino-substituted perethynylated octadehydro[12]- (**5**) and dodecadehydro[18]annulenes (**6**) (*Scheme 2*). Following the serendipitous discovery of perethynylated radiaannulenes (*Scheme 3*) that can be viewed as hybrids between perethynylated dehydroannulenes and expanded radialenes, two series of monocyclic (**7**–**9**; *Scheme 6*) and bicyclic (**10** and **11**; *Scheme 7*) representatives were prepared. Substantial strain in the macrocyclic perimeter of radiaannulene **7** was revealed by X-ray crystal-structure analysis (*Fig. 2*). Nevertheless, mono- and bicyclic radiaannulenes are stable at room temperature in air for months. The opto-electronic properties of both dehydroannulenes and radiaannulenes are substantially enhanced by the introduction of the peripheral anilino donor groups that undergo strong intramolecular charge-transfer interactions with the electron-accepting all-C cores. As a result, the UV/VIS spectra feature intense, bathochromically shifted charge-transfer bands that disappear upon protonation of the anilino moieties and are fully recovered upon neutralization (*Figs. 4–9*). A comparison between anilino-substituted perethynylated dehydroannulenes, expanded radialenes, and radiaannulenes revealed that the efficiency of the intramolecular charge-transfer interaction strongly depends on the structure of the electron-accepting all-C perimeter. Electrochemical investigations (*Table*) demonstrated that the radiaannulenes are particularly powerful electron acceptors. Thus, bicyclic radiaannulene **11**, which possesses eight peripheral 3,5-di(*tert*-butyl)phenyl substituents, is reversibly reduced at -0.83 V in THF (*vs.* Fc^+/Fc), making it a better electron acceptor than buckminsterfullerene C_{60} under comparable conditions.

1. Introduction. – Decades after the seminal work by *Sondheimer* and co-workers [1], dehydroannulenes [2–4] and other types of acetylenic macrocycles [5–14] continue to attract extraordinary interest for various reasons. First, experimental and theoretical studies on these π-electron systems continue to deepen the understanding of the phenomenon of aromaticity [4f][15]. Second, many of these acetylenic chromophores display fascinating opto-electronic properties [16] and third, it has been noted that such C-rich molecules represent sub-structures of two-dimensional all-C networks [17][18] and are potential precursors for the preparation of new molecular C allotropes [3b][19].

In the early 1990s, we started a program on macrocyclic acetylenic scaffolding by using a versatile new family of tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne) building blocks [20]. We prepared per(silylethynylated) octadehydro[12]annulene **1** and dodecadehydro[18]annulene **2**, and demonstrated that the former has antiaromatic character, whereas the latter is aromatic [21] (*Fig. 1*). In another work, we synthesized the first expanded radialenes such as **3** and **4**, members of a new class of

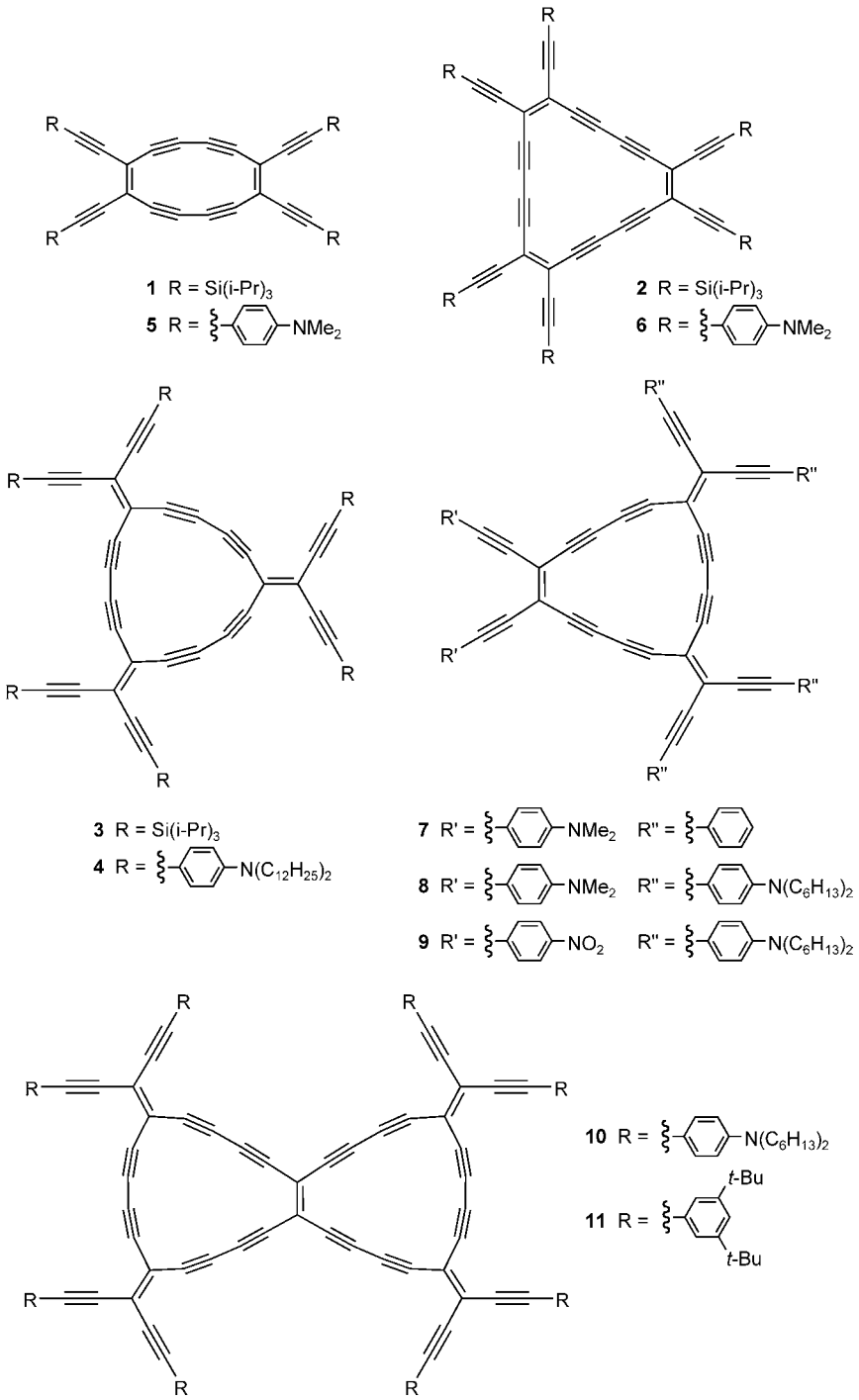


Fig. 1. *Perethynylated dehydroannulenes, expanded radialenes, and radiaannulenes*

cross-conjugated macrocyclic π-chromophores [16][21b][22] (see also [5]). Both perethynylated dehydroannulenes and expanded radialenes were shown by electrochemical investigations to be strong electron acceptors [23], which we explained with the large number of C(sp)-atoms in the large all-C cores. Reduction of the expanded radialenes was found to be particularly facilitated [16b], and this was recently explained by aromaticity enhancement at the stage of the formed mono- and di-anions [24]. Introduction of peripheral *N,N*-dialkylanilino groups into **4** resulted in strong, bathochromically shifted intramolecular charge-transfer transitions [16].

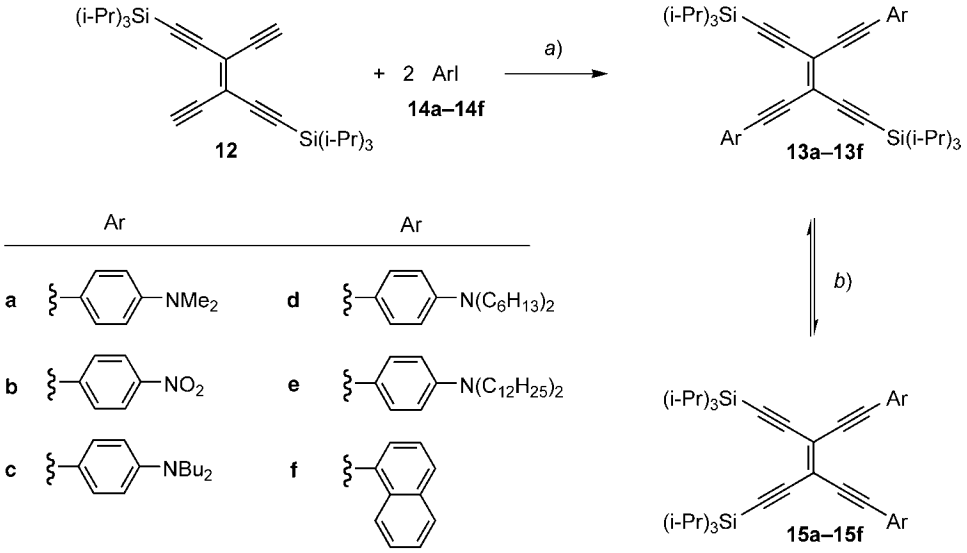
We subsequently became interested in functionalizing dehydroannulenes **1** and **2** with peripheral donor groups in order to investigate whether intramolecular charge-transfer effects are influenced by the aromaticity/antiaromaticity of the macrocyclic perimeters. However, (*Z*)-bisdeprotected TEEs, required for oxidative macrocyclization [25], had been available only by a tedious multistep synthesis including several highly unstable intermediates, which prevented the preparation of functionalized derivatives of **1** and **2**. Here, we report a new, simple photochemical route to (*Z*)-bisdeprotected TEEs that finally enabled the preparation and spectroscopic investigation of the perethynylated dehydroannulenes **5** and **6**, which bear lateral *N,N*-dimethylanilino (DMA) substituents (for a preliminary communication of parts of this work, see [26]). We also report here the synthesis and properties of **7**–**9**, and **10** and **11**, mono- and bicyclic members of a new family of all-C macrocycles, that, from a structural viewpoint, can be regarded as hybrids between the dehydroannulenes and expanded radialenes, and which we have, therefore, christened 'radiaannulenes' (for a preliminary communication, see [27]). The intramolecular charge-transfer properties of the new donor-substituted all-C cores **5**–**11** are discussed in detail.

2. Results and Discussion. – 2.1. *Photochemical Synthesis of (Z)-Bisdeprotected TEEs.* Starting from the *trans*-bisdeprotected TEE **12** [20a], the *trans*-diarylated, *trans*-disilylated TEEs **13a**–**13f** (**13a**, **13b**, and **13e** had been previously reported; see [28]) were prepared in good yield by Pd^0-catalyzed *Sonogashira* cross-coupling with the corresponding aryl iodides **14a**–**14f** (*Scheme 1*).

The compounds were subsequently examined for their ability to undergo photochemical (*E*)/(*Z*) isomerization [29]. For this purpose, solutions of **13a**–**13f** in Et_2O ($c = 2.5$ mM) were irradiated with a water-cooled medium-pressure Hg lamp (125 W) over the course of 2–5 h at room temperature. Doubling of the acetylenic ^{13}C-NMR resonances of the crude products, compared to the spectra of the starting materials, suggested that photochemical (*Z*)/(*E*) isomerization had taken place in all runs (*Scheme 1*). The isomeric mixtures **13a**/**15a** and **13b**/**15b**, respectively, could be readily separated by flash chromatography (FC; SiO_2; CH_2Cl_2/hexane mixtures) to yield *ca.* 40% of the desired (*Z*)-isomer along with *ca.* 50% of the (*E*)-isomer that was used for further photoisomerization. (*E*)-Isomers **15a** and **15b** are air- and light-stable, yellow-orange solids, but they isomerize rapidly in solution when exposed to light. In contrast, the formed isomeric mixtures **13c**/**15c** to **13f**/**15f** could not be separated on a preparative scale (FC); evidently the polarity of the respective (*Z*)- and (*E*)-derivatives is too similar in these cases.

2.2. *Synthesis of the DMA-Substituted Perethynylated Dehydroannulenes* **5** *and* **6**. The $(i\text{-}Pr)_3Si$ protecting groups of **15a** and **15b** were readily cleaved with Bu_4NF in

Scheme 1. *Synthesis of* (E)*-Diaryl-TEEs* **13a**–**13f** *and Photochemical* (E) → (Z) *Isomerization*

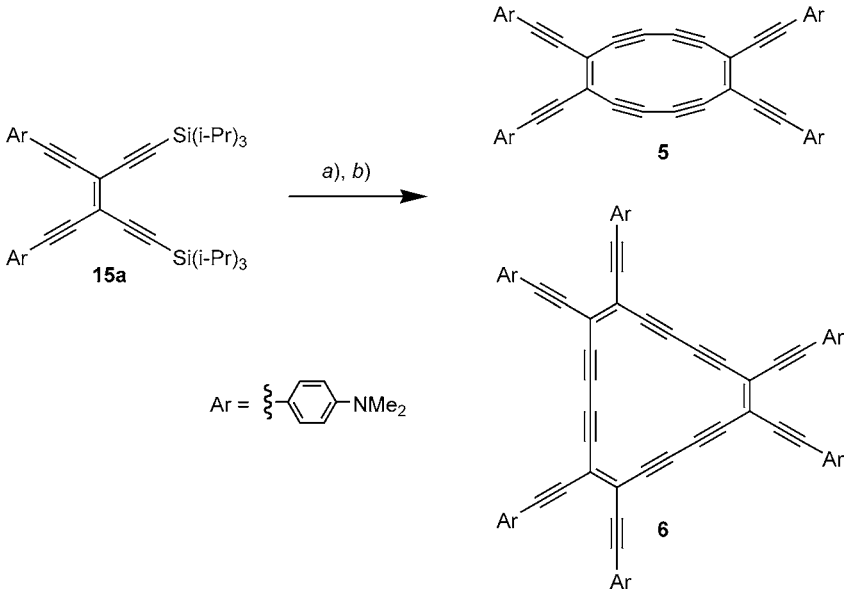


a) $[PdCl_2(PPh_3)_2]$, CuI, $(i\text{-}Pr)_2NH$ (**13a**–**13d**, **13f**) or Et_3N (**13e**), r.t., 16–18 h; 85% (**13a**); 99% (**13b**); 78% (**13c**); 76% (**13d**); 28% (**13e**); 72% (**13f**). *b*) *hv*, Et_2O, r.t., 2–5 h; 41% (**15a**) and 53% (**13a**); 39% (**15b**) and 52% (**13b**); mixtures **13c/15c** to **13f/15f** not separable on a preparative scale.

moist THF, and the tetrabutylammonium salts subsequently removed by filtration through as short plug of SiO_2. The resulting free (*Z*)-enediynes can be handled without problems in solution but deteriorate rapidly in neat form. Hence, they were not characterized and were always freshly prepared before use in subsequent oxidative couplings. *Hay* coupling of **15a** afforded octadehydro[12]annulene **5** and dodecadehydro[18]annulene **6** as deep-purple solids (*Scheme 2*). Interestingly, higher macrocyclic oligomers were not detectable in the matrix-assisted laser-desorption-ionization (MALDI-TOF) mass spectrum (matrix: DCTB = {(2*E*)-3-[4-(*tert*-butyl)phenyl)-2-methylprop-2-enylidene}malononitrile) of the crude product.

The two macrocycles are well soluble in CH_2Cl_2 and $CHCl_3$ but only sparingly soluble in many other organic solvents, which rendered their separation by repetitive FC ($3 \times SiO_2$; CH_2Cl_2/hexane/Et_3N 1:1:0 → 99:0:1) quite difficult. The ratio of the two annulenes is concentration-dependent [21b], as was qualitatively assessed by TLC (SiO_2; CH_2Cl_2/hexane 1:1) of the crude reaction mixture. Nevertheless, even under very high dilution conditions, which favor cyclodimerization over cyclotrimerization, the isolated yield of octadehydro[12]annulene **5** always remained low as a result of its marked instability, which caused a significant loss of product during workup and purification. Careful removal of solvents after workup and chromatography was mandatory; before full evaporation of the solvents, **5** was precipitated with hexane to avoid complete decomposition. Once a solid, the compound could be stored for several days at $-20°$ without significant decomposition. Dodecadehydro[18]annulene **6**, on the other hand, is remarkably stable and can be handled without problem. The identity of the two annulenes was confirmed by ^1H- and ^{13}C-NMR spectroscopy, and high-

Scheme 2. *Synthesis of Perethynylated Dehydroannulenes* **5** *and* **6**



a) Bu_4NF, THF, 0°, 10 min. *b*) CuCl, *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA), air, Me_2CO, r.t., 2 h; 2% (**5**); 22% (**6**).

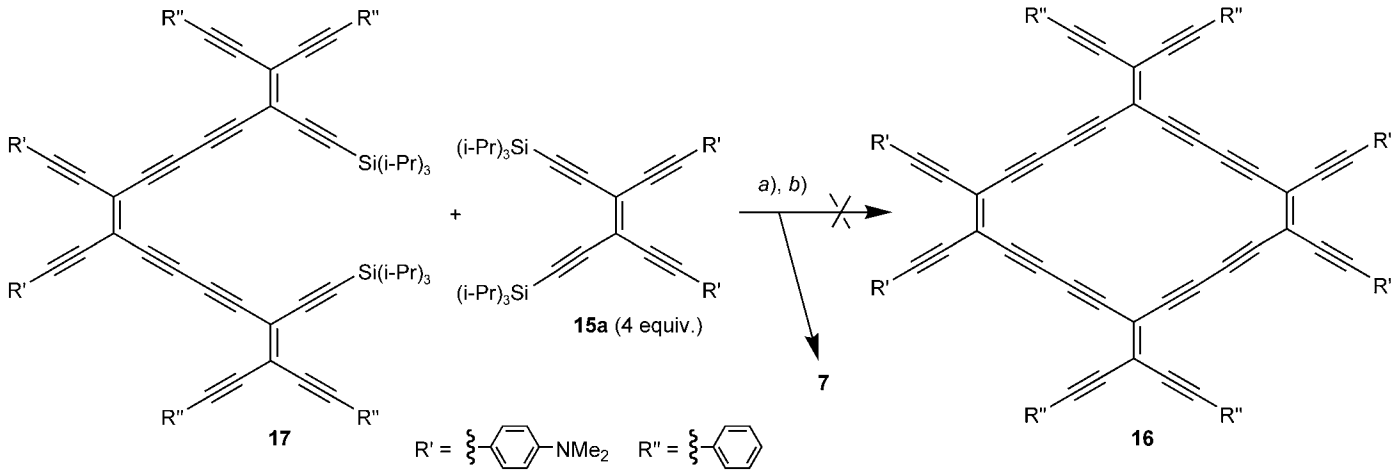
resolution MALDI *Fourier*-transform (FT) mass spectrometry. Attempts to prepare the corresponding dehydroannulenes, which bear electron-withdrawing 4-nitrophenyl groups, starting from **15b**, remained unsuccessful. In all cases, complete decomposition of the starting material was observed.

2.3. *Synthesis of Monocyclic Perethynylated Radiaannulenes.* The discovery of a new class of π-chromophores, radiaannulenes **7**–**9**, occurred during the attempted formation of macrocycle **16** (*Scheme 3*). When trimeric TEE **17** was reacted under oxidative *Hay* coupling conditions with **15a** (4 equiv.), after *in situ* silyl deprotection of the two compounds, the targeted new π-system **16** was not formed, but rather radiaannulene **7** with a smaller, much more strained 16-membered macrocyclic perimeter was obtained (MS, NMR). This observation led to the present systematic investigation of the radiaannulenes.

In view of the solubility problems encountered with the DMA-substituted dehydroannulenes **5** and **6**, we decided to introduce peripheral anilino donors with longer alkyl chains. For this purpose, the new TEE **18** with *N,N*-dihexylanilino groups was prepared from **19** *via* **20** and **21**, by using dibromoolefin **22** [20a] (*Scheme 4*).

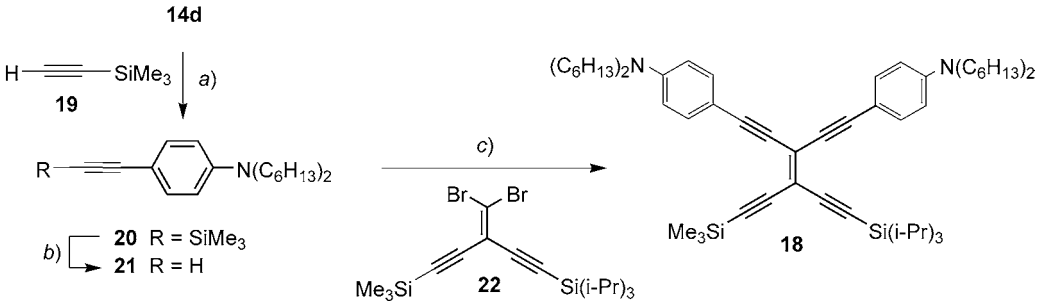
TEEs **18**, **23** [20a], and **24** [28] were subsequently mono-desilylated with K_2CO_3 in MeOH/THF and combined with a solution of *in situ* bisdeprotected (*Z*)-enediynes **15a** and **15b**, respectively, followed by addition of *Hay* catalyst (*Scheme 5*). The use of a six-fold excess of **18**, **23**, or **24** ensured that only the desired mixed TEE trimers **17** and **25**–**27** were formed besides dimers resulting from homo-coupling of the mono-deprotected TEEs.

Scheme 3. *Attempted Synthesis of* **16** *and Unexpected Preparation of Radiaannulene* **7**



a) Bu_4NF, THF. *b*) CuCl, TMEDA, air, Me_2CO.

Scheme 4. *Synthesis of TEE* **18**



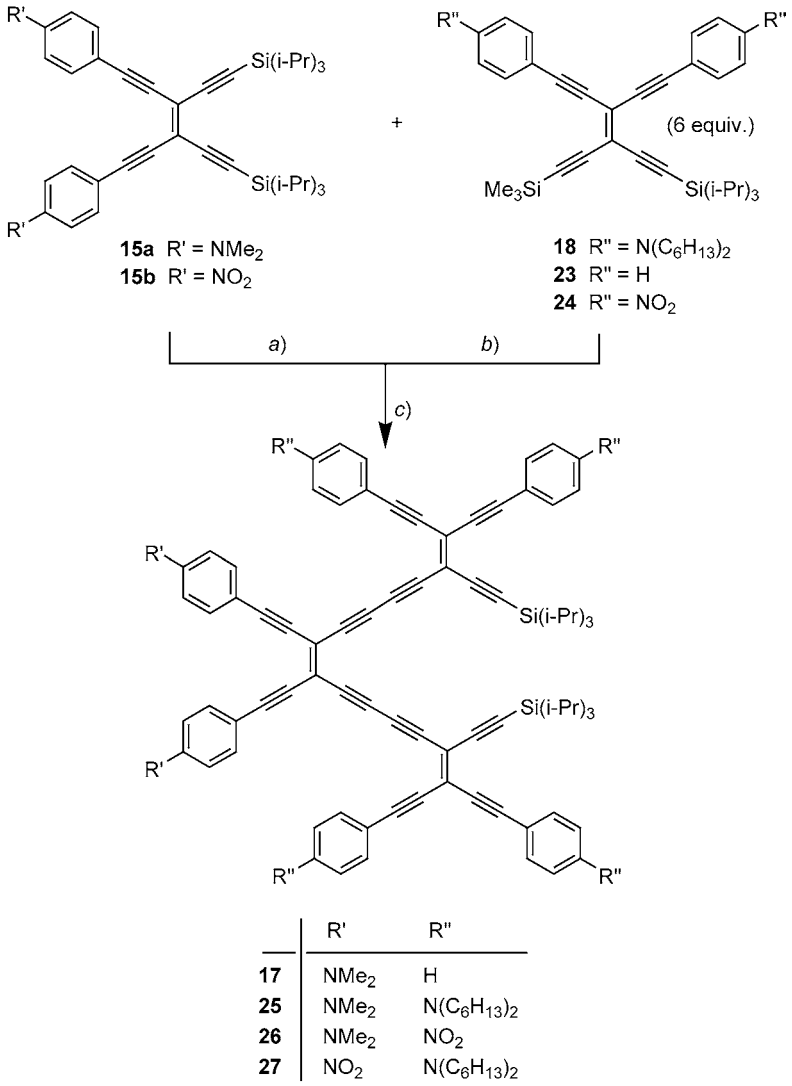
a) $[PdCl_2(PPh_3)_2]$, CuI, $(i\text{-}Pr)_2NH$, r.t., 5 h; 95%. *b*) K_2CO_3, MeOH, THF, r.t, 30 min; 99%. *c*) $[PdCl_2(PPh_3)_2]$, CuI, $(i\text{-}Pr)_2NH$, r.t., 16 h; 69%.

The mixed TEE trimers and homo-dimer side products were readily separated by FC (SiO_2; hexane/AcOEt or hexane/CH_2Cl_2). The brown-colored trimers **17**, **26**, **27**, and purple-colored **25** are air-stable compounds that were fully characterized. After desilylation with Bu_4NF, they were subjected to ring closure under *Hay* coupling conditions (*Scheme 6*). Starting from **17**, **25**, and **27**, the perethynylated radiaannulenes **7**–**9** were isolated as the sole products after purification. They are remarkably stable, brown (**7**) or waxy purple solids (**8** and **9**) that were fully characterized. In the cyclization of **26**, radiaannulene **28** was also formed, as detected by mass spectrometry, but amounts of isolated, purified macrocycle were consistently too small for full characterization. It thus appears that **28** is destabilized by the four electron-withdrawing peripheral 4-nitrophenyl groups.

Single crystals of radiaannulene **7** were obtained by slow diffusion of hexane into a solution in $CHCl_3$. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The X-ray crystal structure [27] shows a virtually planar macrocyclic framework with a mean out-of-plane deviation of 0.040 Å and a maximum deviation of 0.091 Å (C(6); *Fig. 2*). The bond angles of the TEE moiety around the C(1)=C(16) bond are all close to the ideal angle of 120° (117.0°–122.0°). Strain in the 16-membered ring is expressed by bending of the three buta-1,3-diynediyl moieties, with C≡C–C(sp) angles as low as 169.2° and by a deviation of the C(sp)–C(sp^2)–C(sp) angles at the exocyclic ethylene units from ideally 120° to *ca.* 111°. Most strain, however, occurs at the macrocyclic C≡C–C(sp^2) angles C(4)–C(5)–C(6), C(6)–C(7)–C(8), C(9)–C(10)–C(11), and C(11)–C(12)–C(13), with a bending from ideally 180° to *ca.* 164°.

2.4. *Synthesis of Bicyclic Perethynylated Radiaannulenes.* The synthesis of the bicyclic radiaannulenes **10** and **11** started from the parent tetraethynylethene **29** that was prepared *in situ* by treatment of the corresponding tetrakis(trimethylsilyl)-protected derivative in MeOH/THF with K_2CO_3 [20a] (*Scheme 7*). Oxidative *Hay* coupling of **29** with an excess of TEEs **18**, **23**, or **30** [16b], after removal of their Me_3Si protecting groups by protodesilylation, afforded the pentameric TEEs **31**–**33**, respectively, in fair yields (29–39%), together with considerable amounts of homo-coupled TEE dimers. Pentamers **31** and **33** were readily separated from the homo-

Scheme 5. *Synthesis of TEE Hetero-Trimers* **17** *and* **25**–**27**

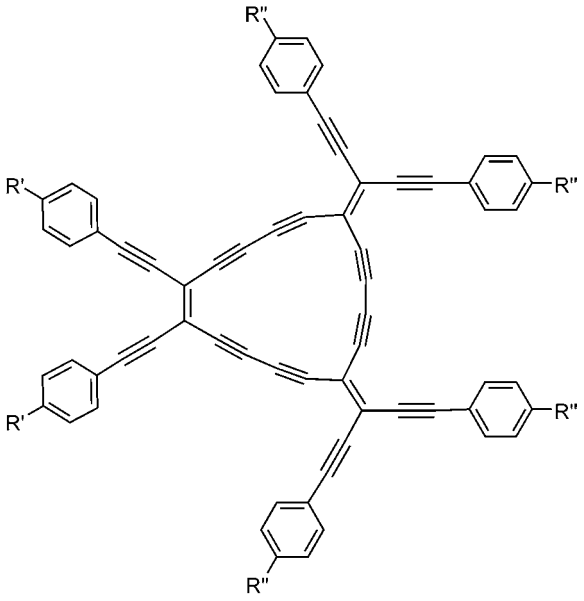


	R'	R"
17	NMe_2	H
25	NMe_2	$N(C_6H_{13})_2$
26	NMe_2	NO_2
27	NO_2	$N(C_6H_{13})_2$

a) Bu_4NF, THF, 0°, 10 min. *b*) K_2CO_3, MeOH/THF, r.t., 2.5 h. *c*) CuCl, TMEDA, air, Me_2CO, r.t., 1–2 h; 57% (**17**); 32% (**25**); 63% (**26**); 32% (**27**).

dimers (formed from **23** and **30**, resp.) by FC (SiO_2; hexane/AcOEt 6:1). Under these conditions, pentamer **32** could not be separated from the undesired homo-dimer (of **18**), but full separation was possible by gel-permeation chromatography (GPC) on a polystyrene resin cross-linked with divinylbenzene (*Bio-Beads 1-SX)* with THF as the eluent. The pentameric TEEs are air-stable, red (**31** and **33**) or brown (**32**) waxy solids that were fully characterized. Compounds **31**–**33** represent the first derivatives of

Scheme 6. *Synthesis of Monocyclic Radiaannulenes*



			R'	R''
17		**7**	NMe_2	H
25	*a*), *b*)	**8**	NMe_2	$N(C_6H_{13})_2$
26	→	**28**	NMe_2	NO_2
27		**9**	NO_2	$N(C_6H_{13})_2$

a) Bu_4NF, THF, 0°, 10 min. *b*) CuCl, TMEDA, air, Me_2CO, r.t., 1–1.5 h; 48% (**7**); 32% (**8**); traces (**28**); 14% (**9**).

tetrakis(buta-1,3-diynyl)ethane ($C_{18}H_4$; 5,6-di(buta-1,3-diynyl)dec-5-ene-1,3,7,9-tetrayne) that had so far been elusive [20a].

Initial attempts to prepare the bicyclic perethynylated radiaannulenes **10** and **34** by silyl deprotection (Bu_4NF) of the pentameric TEEs, followed by intramolecular oxidative *Hay* coupling under conditions identical to those applied to the synthesis of the monocyclic derivatives **7**–**9**, failed. TLC Analysis indicated that the desilylation proceeded smoothly, and that the deprotected pentamers were sufficiently stable for further manipulation. Rather, complete decomposition occurred upon addition of the *Hay* catalyst. Gratifyingly, a slight modification of the *Hay* coupling conditions, with Me_2CO/THF/PhH 1:1:1 instead of pure Me_2CO as solvent allowed the preparation of the octakis(*N,N*-dihexylanilino) derivative **10** that was isolated in 16% yield as a deep-purple, waxy solid. On the other hand, the targeted octaphenyl derivative **34** could still not be isolated, and only decomposition was observed. In sharp contrast, octakis[3,5-di(*tert*-butyl)phenyl] derivative **11** was obtained in excellent yield (88%). Thus, our investigations of perethynylated dehydroannulenes, expanded radialenes [16], and radiaannulenes consistently show that electron-donating peripheral substituents such

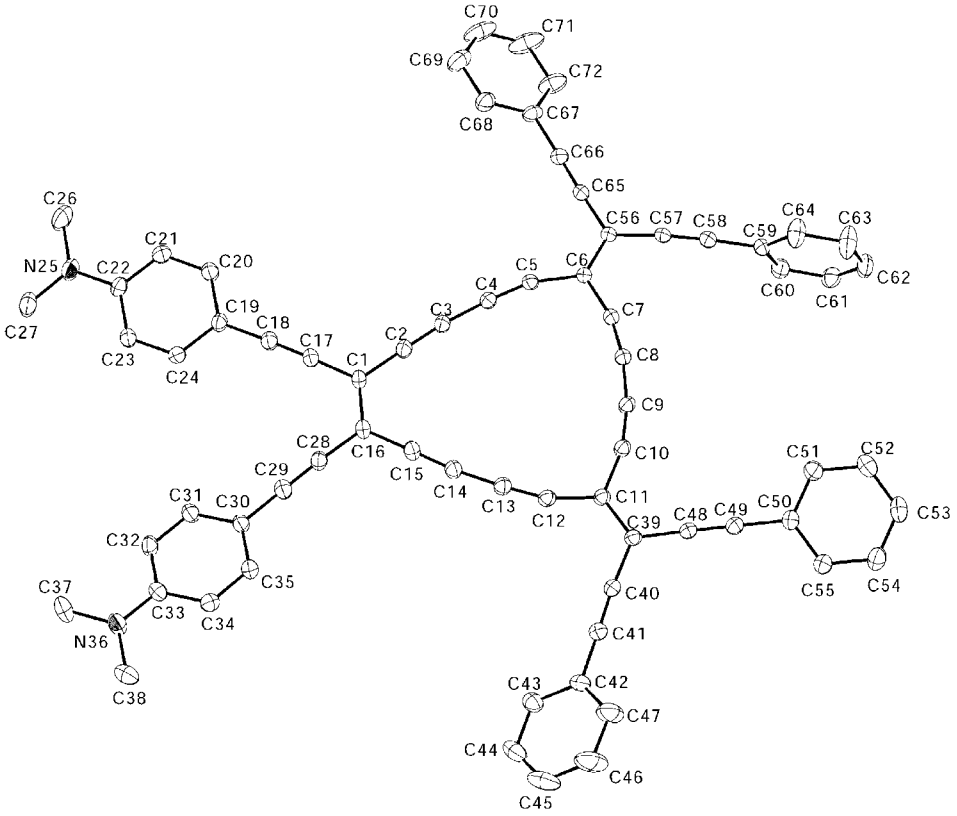
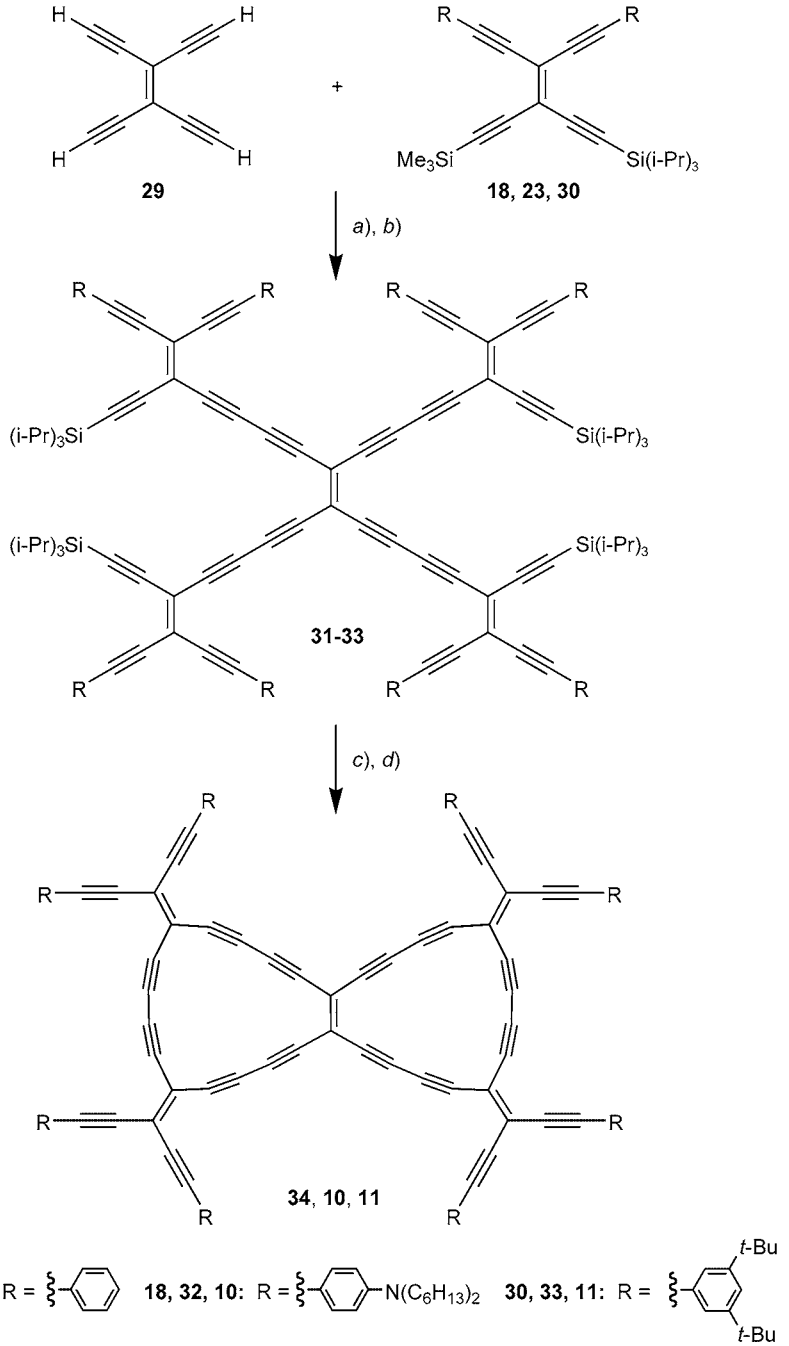


Fig. 2. *ORTEP Plot of* **7** *with arbitrary numbering*. The H-atoms are omitted for clarity. Atomic displacement parameters at 183 K are drawn at the 30% probability level. Selected bond lengths [Å] and bond angles [°]: C(1)–C(2), 1.427(2); C(2)–C(3), 1.204(2); C(3)–C(4) 1.364(2); C(4)–C(5), 1.209(2); C(5)–C(6), 1.423(2); C(6)–C(56), 1.378(2); C(6)–C(7), 1.423(2); C(7)–C(8), 1.206(2); C(8)–C(9), 1.358(2); C(9)–C(10), 1.207(2); C(10)–C(11), 1.425(2); C(11)–C(39), 1.374(2); C(11)–C(12), 1.424(2); C(12)–C(13), 1.207(2); C(13)–C(14), 1.368(3); C(14)–C(15), 1.206(3); C(15)–C(16), 1.421(3); C(1)–C(16), 1.387(3); C(19)–C(20), 1.396(3); C(19)–C(24), 1.398(2); C(20)–C(21), 1.373 (3); C(21)–C(22), 1.406(3); C(22)–C(23), 1.401(3); C(23)–C(24), 1.373(3); C(30)–C(31), 1.390(3); C(30)–C(35), 1.397(3); C(31)–C(32), 1.381(3); C(32)–C(33), 1.403(3); C(33)–C(34), 1.402(3); C(34)–C(35), 1.371(3); C(16)–C(1)–C(2), 120.17(16); C(1)–C(2)–C(3), 178.64(19); C(2)–C(3)–C(4), 174.50(19); C(3)–C(4)–C(5), 175.98(19); C(4)–C(5)–C(6), 163.18(18); C(5)–C(6)–C(7), 111.76(14); C(6)–C(7)–C(8), 164.86(18); C(7)–C(8)–C(9), 169.17(19); C(8)–C(9)–C(10), 170.12(19); C(9)–C(10)–C(11), 163.88(19); C(10)–C(11)–C(12), 111.18(15); C(11)–C(12)–C(13), 162.78(17); C(12)–C(13)–C(14), 176.55(18); C(13)–C(14)–C(15), 174.56(19); C(14)–C(15)–C(16), 178.80 (20); C(15)–C(16)–C(1), 120.99(15).

as dialkylanilino or 3,5-di(*tert*-butyl)phenyl groups provide substantial stabilization to the extended electron-deficient macrocyclic all-C cores. In addition to electronic effects, steric protection may also add to the observed kinetic stability. It should be mentioned that all mono- and bicyclic radiaannulenes isolated in this work are stable at room temperature in the air for months.

Scheme 7. *Synthesis of Bicyclic Radiaannulenes*



a) K_2CO_3, MeOH, THF, r.t. 15–30 min. *b*) CuCl, TMEDA, air, Me_2CO, r.t., 1.5–2.5 h; 39% (**31**, **32**); 29% (**33**). *c*) Bu_4NF, THF, 0°, 10 min. *d*) CuCl, TMEDA, air, Me_2CO/THF/PhH 1:1:1, r.t., 1–2 h; 0% (**34**); 16% (**10**); 88% (**11**).

The proposed structures of **10** and **11** were confirmed by IR, UV/VIS, ^{1}H- and ^{13}C-NMR spectroscopy, and MALDI-TOF mass spectrometry. A high-resolution FT-ICR (ion-cyclotron-resonance) mass spectrum of **11** (matrix: DCTB) features the M^+ ion (*m/z* 2113.3166; calc. for $C_{162}H_{168}$: 2113.3146) as the only significant peak (*Fig. 3*). The ^{13}C-NMR spectrum (125 MHz) of **11** in $CDCl_3$ displays the expected 21 resonances in the C(sp)/C(sp^2) spectral region, thereby confirming the high symmetry (D_{2h}) of the bicyclic structure.

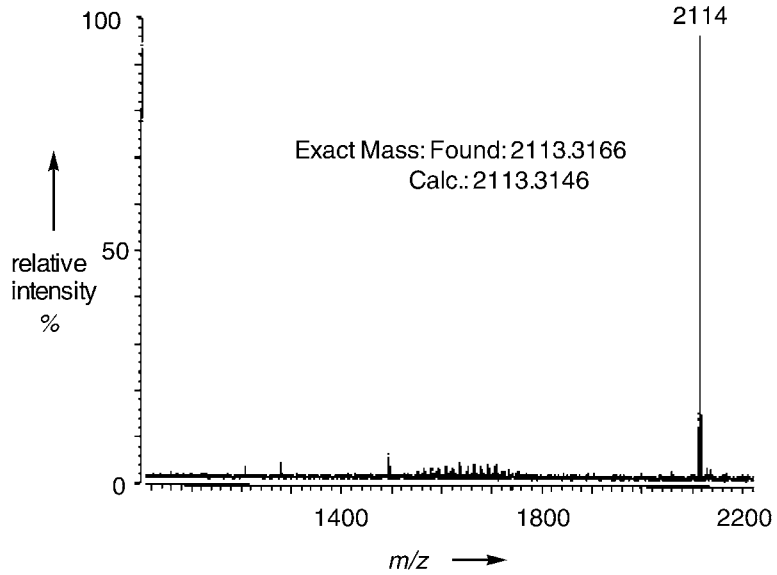


Fig. 3. *High-resolution FT-ICR-MALDI mass spectrum* (positive-ion mode) *of* **11**. Matrix: DCTB.

2.5. *UV/VIS Spectroscopy.* We were interested in exploring whether the aromaticity/antiaromaticity of the new perethynylated dehydroannulenes would affect their capacity to mediate π-electron donor-acceptor conjugation. The UV/VIS spectrum of the aromatic dehydro[18]annulene **6** in $CHCl_3$ (*Fig. 4*) is dominated by an intense, broad longest-wavelength absorption band at $\lambda_{max} = 518$ nm (2.39 eV, $\varepsilon = 105200$ м$^{-1}$ cm^{-1}) and features an end-absorption (around 700 nm, 1.77 eV) that is bathochromically shifted by more than 200 nm compared to that of the corresponding silyl-substituted derivative **2** (480 nm, 2.57 eV) [21]. Upon acidification with TsOH, the color of the solution of **6** changes from purple to yellow, which is the color of the silyl-substituted derivative **2**. Accordingly, the intense absorption at 518 nm disappears nearly completely, and the spectrum becomes strikingly similar to that of **2** with the most-intense band now being shifted to 427 nm (2.90 eV; **2**: 405 nm, 3.06 eV). The residual absorptivity above 500 nm in the acidified solution may be explained by incomplete hexaprotonation. Neutralization with Et_3N completely regenerates the original spectrum. This behavior identifies the intense longest-wavelength absorption at $\lambda_{max} = 518$ nm as a charge-transfer band, resulting from efficient intramolecular charge-transfer between the electron-donating anilino groups and the electron-accepting all-C core.

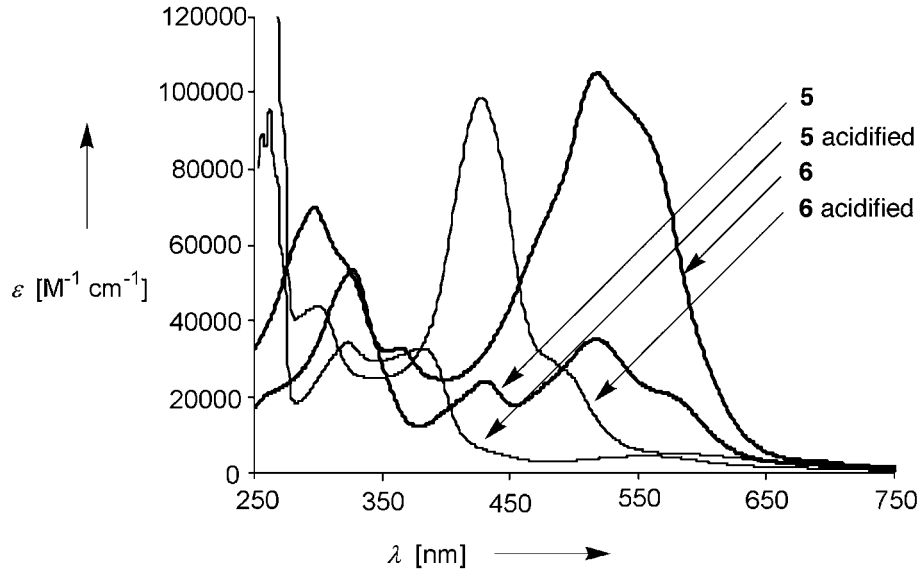


Fig. 4. *UV/VIS Spectra of* **5** *and* **6** *in pure* $CHCl_3$ (thick lines) *and after acidification with TsOH* (thin lines)

In agreement with its antiaromaticity, the per(silylethynylated) dehydro[12]annulene **1** featured a much lower HOMO-LUMO gap (end-absorption near 660 nm, 1.87 eV) than the corresponding aromatic dehydro[18]annulene **2** (480 nm, 2.57 eV), with weak bands between 490 and 620 nm ($\varepsilon = 200$ to 400 M^{-1} cm^{-1}) being responsible for its buckminsterfullerene-type magenta-purple color [21]. In the donor-substituted antiaromatic dehydro[12]annulene **5**, these weak bands are now completely overlapped by an intramolecular charge-transfer transition, featuring the same absorption maximum ($\lambda_{max} = 518$ nm, 2.39 eV, $\varepsilon = 35100$ M^{-1} cm^{-1}) and end-absorption (around 700 nm, 1.77 eV) as the aromatic dehydro[18]annulene **6** (*Fig. 4*). As in the case of **6**, the lowest-energy band disappears nearly completely upon acidification with TsOH and is regenerated upon neutralization with Et_3N. Clearly, both [12]annulene **5** and [18]annulene **6** are capable of mediating π-electron donor-acceptor conjugation in a similar fashion. Interestingly, the intensity of the charge-transfer band of **5** is significantly weaker than that of **6**, even when the smaller number of donor-acceptor conjugation paths is taken into account[1]). This is somewhat surprising since one might expect the charge-transfer to be more efficient in the [12]annulene, as the uptake of electrons reduces the antiaromaticity, whereas, in the case of the [18]annulene, the uptake of electrons is accompanied by a loss of aromaticity. Theoretical calculations might provide further insight into the additional factors that govern the intensity of these electronic transitions.

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[1]) To rule out the possibility that the molar extinction coefficient of **5** is so much lower than that of **6** due to decomposition during the UV/VIS measurements, the homogeneity of **5** was checked after the measurements by ^{1}H-NMR spectroscopy and MALDI-TOF-MS. No indications for any decomposition were obtained.

The anilino-substituted monocyclic perethynylated radiaannulenes **7**–**9** also display intense intramolecular charge-transfer bands in $CHCl_3$ (*Fig. 5*). Upon acidification with CF_3COOH (TFA), these bands disappear, and, not surprisingly, similar UV/VIS spectra are obtained for the three protonated compounds. The residual absorptivity above 550 nm in the case of the hexaanilino derivative **8** may be explained by incomplete hexaprotonation. Upon neutralization with Et_3N, the original spectra are all regenerated.

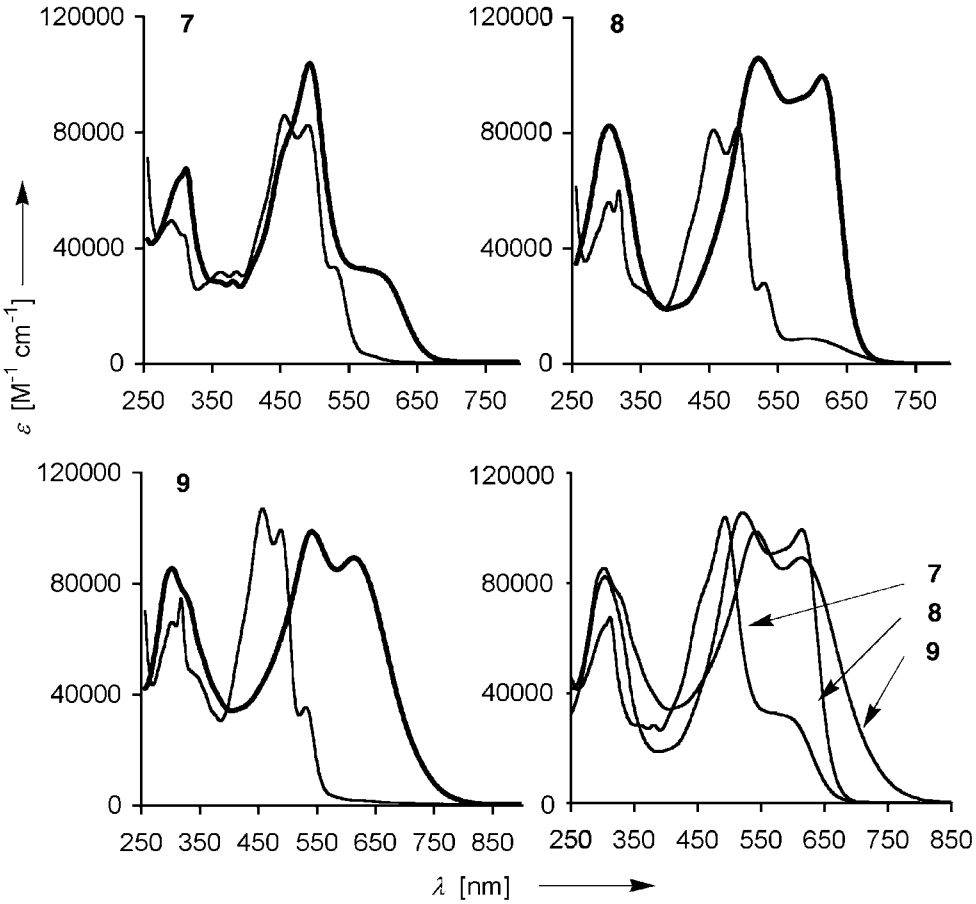

Fig. 5. *UV/VIS Spectra of* **7** (*top left*), **8** (*top right*), *and* **9** (*bottom left*) *in pure* $CHCl_3$ (thick lines) *and after addition of TsOH* (thin lines). Shown on the *bottom right* is a comparison of the spectra of **7**–**9** in $CHCl_3$.

Position and intensity of the CT band are affected by the number of peripheral donor groups. Thus, the CT band of dianilino-substituted **7** is rather weak (λ_{max} = 588 nm (2.11 eV, $\varepsilon = 31900$ м$^{-1}$ cm^{-1})) and detectable only as a shoulder. In contrast, hexaanilino-substituted **8** features a split CT band ($\lambda_{max} = 521$ nm (2.37 eV, ε = 106100 м$^{-1}$ cm^{-1}) and $\lambda_{max} = 615$ nm (2.02 eV, $\varepsilon = 99900$ м$^{-1}$ cm^{-1})), that is much more

intense and bathochromically shifted. The end-absorptions of both compounds, however, are nearly identical (around 700 nm, 1.77 eV).

Introducing two 4-nitrophenyl donor groups in **9**, while maintaining four peripheral anilino donor groups, does not affect the position of the longest-wavelength maximum of the split CT band ($\lambda_{max} = 614$ nm (2.02 eV, $\varepsilon = 89300$ м$^{-1}$ cm^{-1}) as compared with hexa-donor-substituted **8** ($\lambda_{max} = 615$ nm (2.02 eV, $\varepsilon = 99900$ м$^{-1}$ cm^{-1}). UV/VIS Measurements of acyclic TEE dimers with anilino donor substituents had already previously shown that the strong electron-acceptor properties of the all-C cores are only weakly enhanced upon further introduction of additional 4-nitrophenyl acceptor groups [16b]. The end-absorption, however, shifts substantially from *ca.* 700 nm (1.77 eV) in **8** to *ca.* 800 nm (1.55 eV) in **9**.

The intramolecular charge-transfer between the electron-donating amino groups and the electron-accepting all-C core in **7** can be further assessed by determining the quinoid character of the anilino ring. The quinoid character of a benzene ring is expressed by the parameter $\delta r = [(a-b)+(c-b)]/2$, with a, b, and c being the different bond lengths in the ring as shown in *Fig. 6* [30]. In benzene, δr equals zero, whereas values between 0.08 and 0.1 are found for fully quinoid rings. With the bond lengths from the X-ray crystal-structure analysis (*Fig. 2*), an average value $\delta r = 0.0245$ is calculated for the two anilino groups of **7**, indicating considerable quinoid character of the rings and confirming the prevalence of intramolecular charge-transfer (for an even more pronounced quinoid character, see [31]).

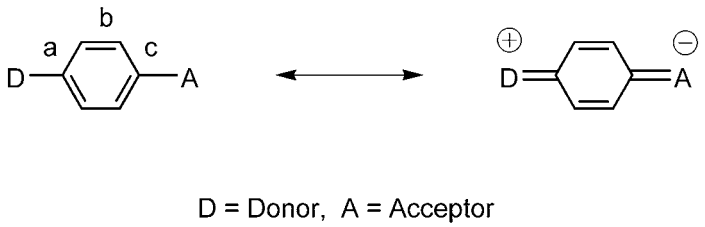

Fig. 6. *Resonance structures of donor-acceptor-substituted benzene rings.* The quinoid character of the benzene ring is a measure of the strength of the intramolecular charge transfer.

A comparison of the UV/VIS spectra of acyclic TEE trimer **25** and radiaannulene **8** reveals that the intramolecular charge-transfer interactions are much more efficient in the macrocyclic compound (*Fig. 7*). Whereas the lowest-energy band with CT character in acyclic **25** appears at $\lambda_{max} = 486$ nm (2.56 eV, $\varepsilon = 98800$ м$^{-1}$ cm^{-1}), the split CT band in macrocyclic **8** is strongly bathochromically shifted ($\lambda_{max} = 521$ nm (2.37 eV, $\varepsilon = 106000$ м$^{-1}$ cm^{-1}) and $\lambda_{max} = 615$ nm (2.02 eV, $\varepsilon = 99900$ м$^{-1}$ cm^{-1})). On the other hand, the longest linear π-conjugation pathways in both compounds are identical, and the optical end-absorptions occur at similar wavelengths (around 700 nm, 1.77 eV). Hence, the fact that the acetylenic core of **8** is a better electron acceptor is a special feature of the macrocyclic scaffold. A similar effect was also observed for the anilino-substituted expanded radialene **4**, which displays a pronounced macrocyclic π-conjugation effect when compared with acyclic TEE dimers possessing the same longest linear π-conjugation pathway [16b].

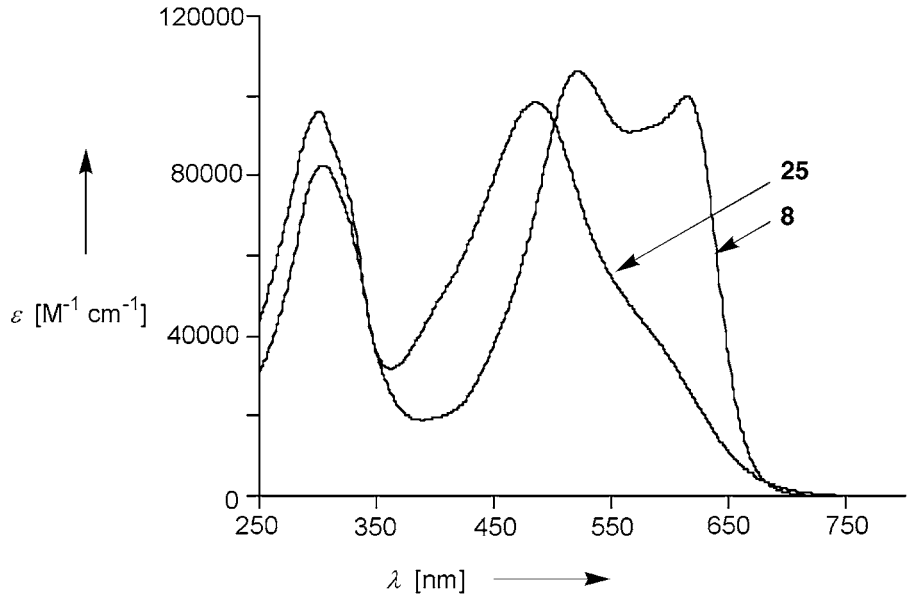

Fig. 7. *UV/VIS Spectra of acyclic TEE trimer* **25** *and radiaannulene* **8** *in* $CHCl_3$

Dehydroannulene **6**, expanded radialene **4**, and radiaannulene **8** all are macrocyclic TEE trimers with the same number of peripheral anilino donor groups. Nonetheless, their UV/VIS spectra display profound differences (*Fig. 8*). The longest-wavelength charge-transfer absorption shifts bathochromically from 518 nm (ε = 105200 M^{-1} cm^{-1}) in **6** (with a shoulder at 533 nm) to 615 nm (ε = 99900 M^{-1} cm^{-1}) in **8**, and to 646 nm (ε = 171000 M^{-1} cm^{-1}) [16b] in **4**, while at the same time, the optical end-absorption also shifts from around 700 nm (in **6** and **8**) to *ca.* 750 nm (in **4**). Furthermore, the exceptionally high molar extinction coefficient of **4**, when compared with **6** and **8**, is noteworthy. Clearly, the capability of macrocyclic TEE scaffolds to mediate charge-transfer interactions depends much on the arrangement of the TEE moieties in the macrocyclic all-carbon perimeter[2]). Future theoretical studies should provide more insight into the observed dependency of intramolecular donor-acceptor interactions from the structure of the macrocyclic acceptor.

Bicyclic radiaannulene **10** with its electron-accepting C_{50} core features the most-intense and the most bathochromically shifted charge-transfer absorptions of all macrocyclic TEE derivatives prepared so far. Its UV/VIS spectrum displays two intense maxima at λ_{max} = 558 nm (2.22 eV, ε = 176700 M^{-1} cm^{-1}) and λ_{max} = 698 nm (1.78 eV, ε = 85900 M^{-1} cm^{-1}; *Fig. 9*). The end-absorption reaches 850 nm (1.46 eV), which is the lowest-energy one known for TEE oligomers. Even expanded [5]- and [6]radialenes with C_{50} and C_{60} cores and ten or twelve peripheral anilino groups, respectively, do not

[2]) It is known that the elongation of the alkyl chains in *N,N*-dialkylanilines can enhance their electron-donating ability [32]. However, we believe that the spectral differences between short-chain **6**, and longer-chain **4** and **8** cannot be explained by such chain-length effects. The CT band maxima are not simply shifted but, instead, entirely new absorption bands appear in the spectra of **4** and **8**.

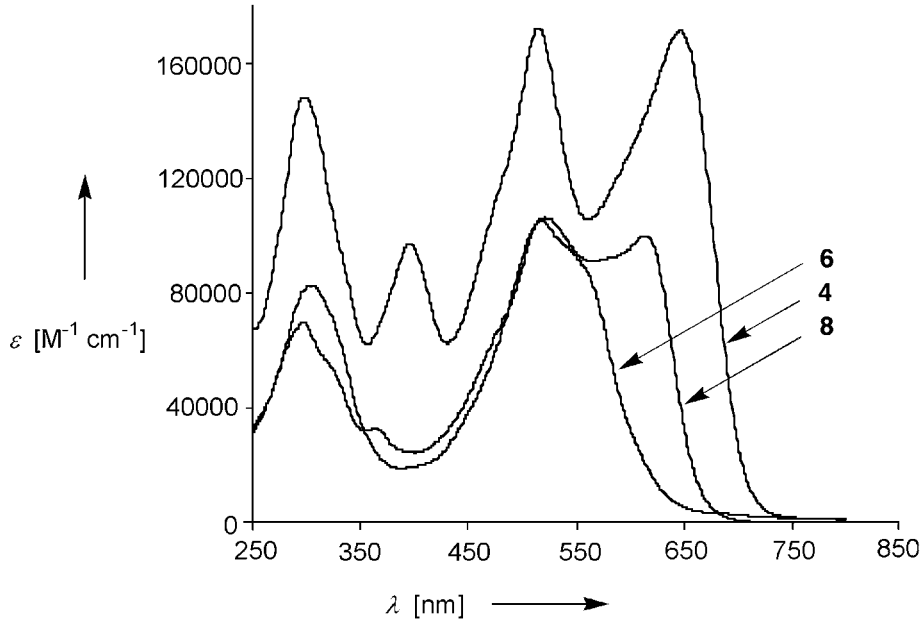

Fig. 8. *Comparison of the UV/VIS spectra of hexaanilino-substituted dehydroannulene* **6**, *expanded radialene* **4**, *and radiaannulene* **8**

feature such low-energy CT transitions and optical end-absorptions [16]. We take this as strong evidence for particularly efficient electronic communication within the bicyclic core of **10**. The CT absorptions of **10** disappear upon acidification and are regenerated unchanged upon neutralization (*Fig. 9*).

2.6. *Electrochemistry.* The electron-accepting power of the novel dehydroannulenes and expanded radialenes was quantified by cyclic voltammetry (CV) and rotating-disc voltammetry (RDV). The measurements were conducted in both THF and CH_2Cl_2 solutions on a glassy-C working electrode with 0.1M Bu_4NPF_6 as the supporting electrolyte. The potentials are referred to the ferricinium/ferrocene (Fc^+/Fc) couple as the internal standard. The results obtained in THF are shown in the *Table*; data obtained in CH_2Cl_2 do not differ much [27].

The CV of anilino-substituted [18]annulene **6** features two well-resolved reversible one-electron reduction steps (−1.36 and −1.72 V in THF; *Table*) demonstrating the electron-acceptor properties of the central C_{30} core. The two reduction steps occur at more negative potentials than those of the silyl-substituted [18]annulene **2** (−1.12 and −1.52 V) [21b][23], which is readily explained by the higher electron density in the all-C core inflicted by the six anilino groups. Additionally, the CV of **6** shows an irreversible third reduction step at −2.27 V (peak potential at 0.1 Vs^{-1}) and a reversible, two-electron oxidation step at +0.25 V; the latter can be attributed to the oxidation of two of the six anilino groups. The remaining anilino groups were oxidized in an irreversible, unresolved peak whose potential was observed at +0.4 V (at 0.1 Vs^{-1}). The redox properties of [12]annulene **5** could, unfortunately, not be studied due to its instability.

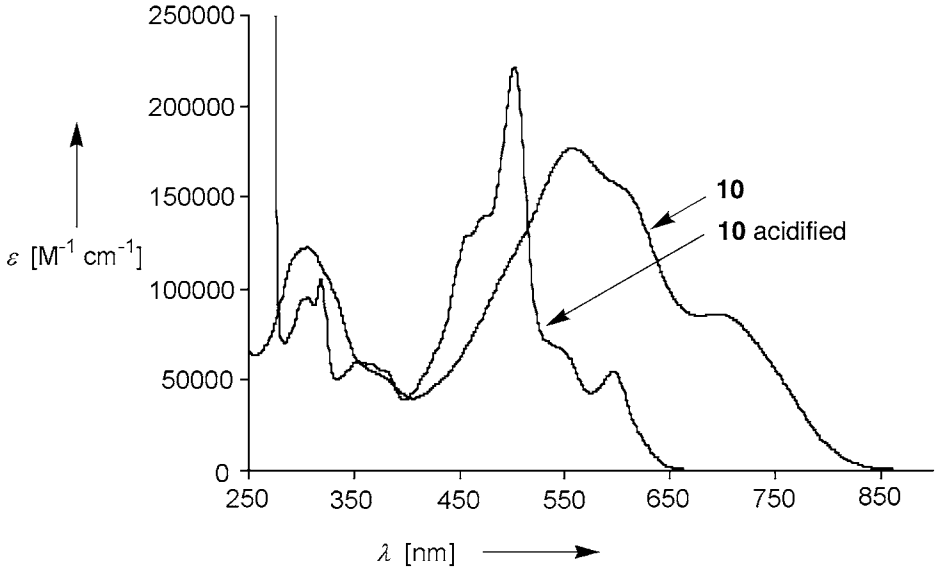

Fig. 9. *UV/VIS Spectra of bicyclic radiaannulene* **10** *in pure* $CDCl_3$ *and upon acidification with TsOH*. The spectrum obtained after neutralization with Et_3N is virtually identical to that shown in pure $CDCl_3$.

The electrochemical behavior of hexaanilino-substituted radiaannulene **8** in THF is characterized by two reversible, one-electron reduction steps at −1.37 and −1.67 V (*Table*), values that are similar to those of **6**, followed by two irreversible reduction steps at −1.85 and −2.15 V. Two irreversible one-electron uptakes are found at +0.38 and +0.54 V that are attributed to the oxidation of the anilino groups. The redox properties of dianilino-substituted radiaannulene **7** are quite similar to those of hexaanilino derivative **8**. Two reversible one-electron reductions are observed at −1.20 and −1.47 V (THF; *Table*), which are less-negative potentials than those of **8** due to the smaller number of electron-donating anilino groups. Several irreversible reduction transfers are detected at −1.86, −1.94, and −2.22 V, and one irreversible two-electron oxidation step is found at +0.34 V for the oxidation of the anilino groups. The tetraanilino-dinitro-substituted radiaannulene **9** displays four reversible one-electron reduction steps at −1.13, −1.38, −1.73, and −1.81 V, followed by an irreversible reduction at −2.33 V (THF; *Table*). An irreversible oxidation step for the anilino groups is observed at +0.44 V. The assignment of the four reversible reductions is not unequivocally possible, but it is likely that the first two reductions occur on the conjugated all-C core and the last two reductions on the 4-nitrophenyl groups [30].

The bicyclic octaanilino-substituted radiaannulene **10** shows three well-separated, one-electron-reduction steps at −0.99, −1.36, and −1.78 V (*Table*). Remarkably, these potentials are less negative than those measured for hexaanilino-substituted macrocycles such as **6** and **8**, which already indicates that the bicyclic all-C core has exceptional electron-acceptor properties. Two irreversible oxidation peaks for the anilino groups are observed at +0.48 and +0.57 V. Bicyclic radiaannulene **11**, lacking anilino donor groups, displays an extremely low first reduction potential at −0.83 V

Table. *Cyclic Voltammetry (CV) and Rotating-Disk-Voltammetry Data in THF (+ 0.1M Bu_4NPF_6)*. Potentials *vs.* Fc/Fc^+. Working electrode: glassy-C electrode; counter electrode: Pt; reference electrode: Ag/AgCl. Scan rate: 0.1 V s^{-1}

	Cyclic Voltammetry			Rotating-Disk Voltammetry	
	E°/V[a])	ΔE_p/mV	E_p/V[b])	$E_{1/2}$/V	Slope/mV
6	+ 0.25	120		–	–
	– 1.36	75			
	– 1.72	100			
			– 2.27		
7			+ 0.34	+ 0.41 (2 e^-)	60
	– 1.20	90		– 1.22 (1 e^-)	70
	– 1.47	80		– 1.53 (1 e^-)	80
			– 1.86	– 1.91	
			– 1.94		
			– 2.22		
8			+ 0.54	+ 0.40 (2 e^-)	80
			+ 0.38	+ 0.28 (2 e^-)	35
	– 1.37	90		– 1.29 (1 e^-)	80
	– 1.67	90		[c])	
			– 1.85		
			– 2.15		
9			+ 0.44	[c])	
	– 1.13	70		– 1.12 (1 e^-)	80
	– 1.38	80		– 1.38 (1 e^-)	100
	– 1.73	60		– 1.73 (2 e^-)	120
	– 1.81	70	– 2.33		
10			+ 0.57		
			+ 0.48	+ 0.37 (8 e^-)	80
	– 0.99	80		– 1.00 (1 e^-)	80
	– 1.36	80		– 1.37 (1 e^-)	70
	– 1.78	90		– 1.87 (1 e^-)	
11	– 0.83	100		– 0.89	120
	– 1.19	125		[c])	
	– 1.62	125			
	– 1.75	125			

[a]) $E^\circ = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b]) E_p = Irreversible peak potential. [c]) Unresolved further waves.

(*Table*). This is the lowest value observed for any macrocyclic TEE oligomer and is even lower than the first reduction potential of buckminsterfullerene C_{60} (– 1.02 V under comparable conditions [20]), which is touted as a very good electron acceptor.

3. Conclusions. – Acetylenic molecular scaffolding by using tetraethynylethene building blocks provides access to unprecedented families of all-C macrocycles featuring exceptional properties. In this paper, a new class of all-C sheets, the perethynylated mono- (C_{30} core) and bicyclic (C_{50} core) radiaannulenes are introduced for the first time. These compounds can be stored at room temperature in the air for months without decomposition. Electrochemical (CV and RDV) analysis demonstrates

that these macrocycles are exceptional electron acceptors. Thus, bicyclic radiaannulene **11**, possessing eight peripheral 3,5-di(*tert*-butyl)phenyl substituents, is reversibly reduced at -0.83 V in THF (*vs.* Fc^+/Fc), making it a better electron acceptor than buckminsterfullerene C_{60} under comparable conditions. In previous work, we had shown that peripheral dialkylanilino substituents dramatically enhance the stability and optoelectronic properties of perethynylated expanded radialenes [16]. Further evidence in this direction was obtained in this work. A novel photochemical access to (*Z*)-bisdeprotected TEEs paved the way to the synthesis of anilino-substituted dehydroannulenes **5** and **6**. Both mono- and bicyclic radiaannulenes with peripheral anilino groups were also prepared in this work. The combined study of all of these anilino-substituted acetylenic macrocycles (annulenes, radialenes, radiaannulenes) allows the following conclusions concerning the beneficial effects of the donor groups: *i*) they increase the solubility of the macrocycles, *ii*) they provide remarkable stabilization of the electron-deficient all-C cores against nucleophilic attack and cycloadditions, and *iii*) they undergo strong intramolecular charge-transfer interactions with the electron-accepting all-C cores, resulting in intense, bathochromically shifted CT bands. The efficiency of the charge-transfer interactions strongly depends on the structure of the all-C core, which should be further clarified by a future theoretical study. Facile synthetic protocols, high stability, and fascinating physical properties make the radiaannulenes interesting advanced materials for optoelectronic applications. Accordingly, the investigation of their nonlinear optical and two-photon absorption properties is now being pursued in collaboration.

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Experimental Part

General. Reagents and solvents were purchased as reagent grade and used without further purification. THF was freshly distilled under N_2 from sodium/benzophenone. *Hay* catalyst is referred to as a freshly prepared solution of CuCl (100 mg, 1.0 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA; 0.15 ml, 116 mg, 1.0 mmol) in Me_2CO or CH_2Cl_2 (25 ml). Iodoarenes **14b** and **14f** were commercially available; **14a** [34] and **14e** [28] as well as TEEs **12** [20a], **13b** [28], **13e** [28], and **30** [16b] were prepared according to literature procedures. All reactions were conducted in standard, oven-dried glassware under an inert atmosphere (N_2 or Ar), except for the *Hay* coupling reactions, which were conducted exposed to air. Evaporation and concentration *in vacuo* was performed at water aspirator pressure; drying *in vacuo* at 10^{-2} Torr. Flash column chromatography (FC): SiO_2-*60* (230–400 mesh ASTM, 0.040–0.063 mm; *E. Merck*). TLC: glass sheets coated with SiO_2-*60* F_{254} from *E. Merck*; visualization with a UV lamp (254 or 366 nm). Prep. gravity GPC: *BIO-RAD Beads S-X1* (pore size 200–400 μm) as stationary phase at ambient pressure and temp. M.p.: *Büchi B-540* melting-point apparatus in open capillaries; uncorrected. Some melting/decomposition points could not be determined due to the dark color of the solid. UV/VIS Spectra: *Cary-5* spectrometer; absorption maxima in nm and molar extinction coefficients in M^{-1} cm^{-1}; sh = shoulder. IR Spectra: *Perkin-Elmer FT-IR 1600* spectrometer; KBr pellet, soln. in $CHCl_3$, or film. ^{1}H-NMR Spectra: *Varian GEMINI 300* spectrometer at 300 MHz in $CDCl_3$ or $(CD_3)_2NCDO$; chemical shift δ [ppm], coupling constant *J* (Hz); residual protic solvent $CHCl_3$ (7.24 ppm) and $(CHD_2)_2NCDO$ (2.74 ppm) used as internal reference. ^{13}C-NMR Spectra: *Varian GEMINI 300* spectrometer at 75 MHz or *Varian GEMINI 500* instrument at 125 MHz; $CDCl_3$ (77.00 ppm) and $(CD_3)_2NCDO$ (30.1 ppm) as reference signals. EI-MS (70 eV): *VG-Tribid* instrument; MALDI-TOF-MS: *Bruker Reflex* with DCTB ({(2*E*)-3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidene}malononitrile) as matrix; high-resolution (HR) MALDI-MS: *Ion Spec Ultima® FT-ICR* spectrometer (with DCTB as matrix). Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH Zürich, with a *LECO CHN/900* instrument.

Electrochemistry. The electrochemical experiments were carried out at 20° in THF or CH_2Cl_2 containing 0.1M Bu_4NPF_6 in a classical three-electrode cell. The working electrode was a glassy C disk electrode (3 mm in diameter) used either in a motionless mode for CV (0.1 to 10 V s^{-1}) or as rotating-disk electrode for RDV. The counter electrode was Pt electrode, and the pseudo-reference electrode used was a Pt wire. All potentials are referenced to the ferricinium/ferrocene (Fc^+/Fc) couple used as an internal standard. The accessible range of potentials on the glassy C electrode was +1.4 to −2.4 V *vs.* Fc^+/Fc in CH_2Cl_2 and +1.1 to −2.9 V *vs.* Fc^+/Fc in THF. The electrochemical cell was connected to a computerized multipurpose electrochemical device *AUTOLAB* (*Eco Chemie BV*, NL-Utrecht) by the *GPSE* software running on a personal computer.

N,N-*Dibutyl-4-iodoaniline* (**14c**). To 4-iodoaniline (2.0 g, 9.1 mmol) and 1-iodobutane (3.5 ml, 5.5 g, 30.1 mmol) in DMF (25 ml), Na_2CO_3 (1.7 g, 16.0 mmol) was added, and the mixture was heated to 95° for 20 h. After cooling to r.t., the mixture was poured into H_2O (100 ml) and extracted with AcOEt (2 × 100 ml). The combined org. layers were washed with H_2O (2 × 50 ml) and sat. aq. NaCl soln. (50 ml), dried ($MgSO_4$), and evaporated *in vacuo*. Filtration of the residue through a plug (SiO_2; hexane) gave **14c** (2.9 g, 96%). Colorless oil. IR (film): 3085, 2954, 1587, 1496, 1368, 801. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.92 (*t*, *J* = 7.4, 6 H); 1.32 (*m*, 4 H); 1.50 (*m*, 4 H); 3.20 (*t*, *J* = 7.7, 4 H); 6.39 (*d*, *J* = 9.2, 2 H); 7.39 (*d*, *J* = 9.2, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.10; 20.38; 29.25; 50.72; 75.23; 113.89; 137.45; 147.42. EI-MS: 331 (40, M^+), 288 (100, $[M - C_3H_7]^+$). Anal. calc. for $C_{14}H_{22}IN$ (331.24): C 50.77, H 6.69, N 4.23; found: C 50.71, H 6.62, N 4.26.

N,N-*Dihexyl-4-iodoaniline* (**14d**). To 4-iodoaniline (2.0 g, 9.1 mmol) and 1-iodohexane (4.5 ml, 6.17 g, 30.1 mmol) in DMF (25 ml), Na_2CO_3 (1.7 g, 16.0 mmol) was added, and the mixture was heated to 95° for 20 h. After cooling to r.t., the mixture was poured into H_2O (100 ml) and extracted with AcOEt (2 × 100 ml). The combined org. layers were washed with H_2O (2 × 50 ml) and sat. aq. NaCl soln. (50 ml), dried ($MgSO_4$), and evaporated *in vacuo*. Filtration of the residue through a plug (SiO_2; hexane) afforded **14d** (3.1 g, 88%). Colorless oil. IR (film): 3080, 2925, 1589, 1496, 1367, 802. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.88 (*t*, *J* = 6.6, 6 H); 1.28 (*m*, 12 H); 1.53 (*m*, 4 H); 3.19 (*t*, *J* = 7.7, 4 H); 6.38 (*d*, *J* = 9.0, 2 H); 7.39 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.14; 22.74; 26.84; 27.06; 31.75; 50.98; 75.27; 113.84; 137.42; 147.36. EI-MS: 387 (35, M^+), 316 (100, $[M - C_5H_{11}]^+$). Anal. calc. for $C_{18}H_{30}IN$ (387.35): C 55.82, H 7.81, N 3.62; found: C 55.80, H 7.86, N 3.76.

N,N-*Dimethyl-4-{(3*E*)-6-[4-(dimethylamino)phenyl]-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyn-1-yl}benzenamine* (**13a**) [28]. To a degassed soln. of **14a** [34] (340 mg, 1.38 mmol) in $(i\text{-}Pr)_2NH$ (15 ml), **12** [20a] (300 mg, 0.68 mmol), $[PdCl_2(PPh_3)_2]$ (30 mg, 0.043 mmol), and CuI (15 mg, 0.079 mmol) were added, and the mixture was stirred for 18 h at r.t. Hexane (50 ml) was added to the deep-red suspension that was filtered through a plug (SiO_2; CH_2Cl_2). The brown solid obtained by evaporation *in vacuo* was purified by FC (SiO_2; hexane/CH_2Cl_2 1:1) to give **13a** (388 mg, 85%; [28]: 43%). Orange solid with anal. data identical to those reported in [28].

N,N-*Dibutyl-4-{(3*E*)-6-[4-(dibutylamino)phenyl]-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyn-1-yl}benzenamine* (**13c**). To a degassed soln. of **14c** (190 mg, 0.58 mmol) in $(i\text{-}Pr)_2NH$ (10 ml), **12** [20a] (130 mg, 0.29 mmol), $[PdCl_2(PPh_3)_2]$ (20 mg, 0.03 mmol), and CuI (10 mg, 0.05 mmol) were added, and the mixture was stirred for 18 h at r.t. Hexane (50 ml) was added to the deep-red suspension that was filtered through a plug (SiO_2; CH_2Cl_2). The brown solid obtained by evaporation *in vacuo* was purified by FC (SiO_2; hexane/CH_2Cl_2 6:1) to yield **13c** (190 mg, 78%). Orange solid. Mp 73.0–75.4°. UV/VIS ($CHCl_3$): 299 (40000), 476 (46000). IR (KBr): 2928, 2863, 2195, 2138, 1602, 1520. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.96 (*t*, *J* = 7.2, 12 H); 1.13 (*s*, 42 H); 1.35 (*m*, 8 H); 1.56 (*m*, 8 H); 3.27 (*t*, *J* = 7.8, 8 H); 6.53 (*d*, *J* = 8.9, 4 H); 7.29 (*d*, *J* = 8.9, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.49; 14.10; 18.83; 20.40; 29.45; 50.70; 86.92; 99.87; 100.12; 104.58; 108.49; 110.92; 115.55; 133.06; 148.05. EI-MS: 842 (100, M^+). Anal. calc. for $C_{56}H_{86}N_2Si_2$ (843.48): C 79.74, H 10.28, N 3.32; found: C 79.69, H 10.30, N 3.23.

N,N-*Dihexyl-4-{(3*E*)-6-[4-(dihexylamino)phenyl]-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyn-1-yl}benzenamine* (**13d**). To a degassed soln. of **14d** (230 mg, 0.59 mmol) in $(i\text{-}Pr)_2NH$ (10 ml), **12** [20a] (130 mg, 0.29 mmol), $[PdCl_2(PPh_3)_2]$ (20 mg, 0.03 mmol), and CuI (10 mg, 0.05 mmol) were added, and the mixture was stirred for 18 h at r.t. Hexane (20 ml) was added to the deep-red suspension that was filtered through a plug (SiO_2; CH_2Cl_2). The brown solid obtained by evaporation *in vacuo* was purified by FC (SiO_2; hexane/CH_2Cl_2 4:1) to provide **13d** (210 mg, 76%). Orange solid. Mp 75.1–75.9°. UV/VIS ($CHCl_3$): 300 (36000), 476 (42000). IR (KBr): 2928, 2861, 2195, 2138, 1602, 1520. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.92 (*t*, *J* = 6.3, 12 H); 1.15 (*s*, 42 H); 1.33 (*m*, 24 H); 1.59 (*m*, 8 H); 3.28 (*t*, *J* = 7.5, 8 H); 6.54 (*d*, *J* = 9.0, 4 H); 7.31 (*d*, *J* = 9.0, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.48; 14.14; 18.82; 22.77; 26.87; 27.26; 31.77; 50.97; 86.92; 99.82; 100.12; 104.59; 108.46; 110.89; 115.57; 133.05; 148.01. MALDI-MS: 954 (100, M^+). Anal. calc. for $C_{64}H_{102}N_2Si_2$ (955.69): C 80.43, H 10.76, N 2.93; found: C 80.20, H 10.87, N 2.85.

*Triisopropyl{(3*E*)-6-(naphthalen-1-yl)-3-[(naphthalen-1-yl)ethynyl]-4-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyn-1-yl}silane* (**13f**). To a degassed soln. of **14f** (384 mg, 1.51 mmol) in $(i\text{-}Pr)_2NH$ (20 ml), **12** [20a] (330 mg, 0.76 mmol), $[PdCl_2(PPh_3)_2]$ (40 mg, 0.06 mmol), and CuI (20 mg, 0.1 mmol) were added, and the mixture was stirred for 16 h at r.t. Hexane (50 ml) was added to the thick orange suspension that was filtered through a plug (SiO_2; hexane/CH_2Cl_2). The orange solid obtained by evaporation *in vacuo* was purified by recrystallization from EtOH/PhMe to give **13f** (377 mg, 72%). Mp 182–183°. UV/VIS ($CHCl_3$): 306 (23700), 408 (35800), 429 (33800). IR (KBr): 2936, 2857, 2196, 2140, 1457, 1399, 1189, 1147, 1088, 996, 881, 794, 766, 677, 663, 643, 582. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*s*, 42 H); 7.44 (*m*, 2 H); 7.53 (*m*, 4 H); 7.71 (*m*, 2 H); 7.85 (*m*, 4 H); 8.41 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.44; 18.81; 92.79; 96.99; 102.38; 103.76; 116.82; 120.24; 125.04; 126.30; 126.41; 126.81; 128.12; 129.43; 130.59; 133.01; 133.33. EI-MS: 688 (100, M^+). Anal. calc. for $C_{48}H_{56}Si_2$ (689.14): C 83.66, H 8.19; found: C 83.49, H 8.33.

N,N-*Dimethyl-4-{(3*Z*)-6-[4-(dimethylamino)phenyl]-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyn-1-yl}benzenamine* (**15a**). A soln. of **13a** (300 mg, 0.44 mmol) in Et_2O (180 ml) was irradiated with a medium-pressure Hg lamp (125 W) for 2 h at r.t. Evaporation *in vacuo* gave an orange solid that was subjected to FC (SiO_2; hexane/CH_2Cl_2 2:1) to yield **15a** (123 mg, 41%) besides recovered **13a** (160 mg, 53%). Orange solid. Mp 159–160°. UV/VIS ($CHCl_3$): 278 (sh, 27400), 299 (31100), 400 (30000), 460 (31300). IR (KBr): 2941, 2861, 2179, 2126, 1606, 1520, 1367. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.11 (*s*, 42 H); 2.98 (*s*, 12 H); 6.61 (*d*, $J = 9.0$, 4 H); 7.36 (*d*, $J = 9.0$, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.47; 18.84; 40.24; 87.38; 100.18; 100.28; 104.27; 109.80; 111.66; 115.41; 132.86; 150.22. EI-MS: 674 (100, M^+). Anal. calc. for $C_{44}H_{62}N_2Si_2$ (675.16): C 78.28, H 9.26, N 4.15; found: C 78.27, H 9.27, N 4.15.

*Triisopropyl{(3*Z*)-3,4-bis[(4-nitrophenyl)ethynyl]-6-(triisopropylsilyl)hex-3-ene-1,5-diyne-1-yl}silane* (**15b**). A soln. of **13b** [28] (75 mg, 0.11 mmol) in Et_2O (160 ml) was irradiated with a medium-pressure Hg lamp (125 W) for 5 h at r.t. Evaporation *in vacuo* provided a residue that was subjected to FC (SiO_2; hexane/CH_2Cl_2 2:1) to give **15b** (29 mg, 39%) and recovered **13b** (37 mg, 52%). Yellow solid. Mp 172–173°. UV/VIS ($CHCl_3$): 318 (36600), 404 (30300). IR (KBr): 2941, 2863, 1592, 1519, 1340, 850, 828, 683. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.12 (*s*, 42 H); 7.59 (*d*, $J = 8.9$, 4 H); 8.21 (*d*, $J = 8.9$, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.33; 18.72; 91.71; 96.21; 102.45; 104.51; 117.88; 123.48; 129.03; 132.40; 147.33. EI-MS: 678 (100, M^+). Anal. calc. for $C_{40}H_{50}N_2O_4Si_2$ (679.02): C 70.76, H 7.42, N 4.13; found: C 70.81, H 7.56, N 4.22.

*4,4′,4″,4‴-[Cyclododeca-1,7-diene-3,5,9,11-tetrayne-1,2,7,8-tetrayltetrakis(ethyne-2,1-diyl)]tetrakis[*N,N-*dimethylaniline]* (**5**) *and 4,4′,4″,4‴,4⁗,4⁗′-[Cyclooctadeca-1,7,13-triene-3, 5,9,11,15,17-hexayne-1,2,7,8,13,14-hexaylhexakis(ethyne-2,1-diyl)]hexakis[*N,N-*dimethylaniline]* (**6**). To a cooled (0°) soln. of **15a** (100 mg, 0.148 mmol) in moist THF (10 ml), Bu_4NF (0.44 ml of a 1.0M soln. in THF, 0.44 mmol) was added. After stirring for 10 min, TLC control indicated that the deprotection was complete. CH_2Cl_2 (50 ml) was added, and the soln. was filtered through a plug (SiO_2; CH_2Cl_2). Evaporation *in vacuo* provided a brownish oil that was dissolved in Me_2CO (150 ml). *Hay* catalyst (3 ml) was added, and the mixture was stirred under air at r.t. for 2 h, after which time TLC control indicated that all the deprotected starting material had been consumed. The deep-purple soln. was filtered through a plug (SiO_2) and concentrated *in vacuo* to a volume of *ca.* 100 ml. Hexane (200 ml) was added, and the soln. was once again concentrated to *ca.* 100 ml, resulting in the formation of a black precipitate. The remaining soln. was decanted off, and the residue was subjected to FC (hexane/CH_2Cl_2 1:1 → CH_2Cl_2/Et_3N 10:1) to yield **5** (1.1 mg, 2.1%) and **6** (11.8 mg, 22%).

Data of **5**: Deep-purple solid. UV/VIS ($CHCl_3$): 327 (53400), 431 (24100), 518 (35100), 566 (sh, 20600). ^{1}H-NMR (500 MHz, $(CD_3)_2NCDO$): 3.04 (*s*, 24 H); 6.78 (*d*, $J = 9.0$, 8 H); 7.36 (*d*, $J = 9.0$, 8 H). ^{13}C-NMR (125 MHz, $(CD_3)_2NCDO$): 39.92; 85.28; 87.85; 95.32; 107.12; 107.62; 112.66; 120.83; 133.80; 152.14. MALDI-TOF-MS: 720 (100, M^+). HR-FT-ICR-MALDI-MS: 720.3253 (M^+; $C_{52}H_{40}N_4^+$; calc. 720.3253).

Data of **6**: Deep-purple solid. UV/VIS ($CHCl_3$): 297 (69800), 366 (32600), 518 (105200), 533 (sh, 99000). IR (KBr): 3037, 2990, 2140, 1617, 1456, 815, 797, 552. ^{1}H-NMR (500 MHz, $(CD_3)_2NCDO$): 3.10 (*s*, 36 H); 6.89 (*d*, $J = 9.0$, 12 H); 7.63 (*d*, $J = 9.0$, 12 H). ^{13}C-NMR (125 MHz, $(CD_3)_2NCDO$): 39.98; 83.22; 86.23; 87.26; 107.71; 107.90; 112.76; 115.84; 134.03; 152.26. MALDI-TOF-MS: 1080 (100, M^+). HR-FT-ICR-MALDI-MS: 1080.4884 (M^+, $C_{78}H_{60}N_6^+$; calc. 1080.4879). Anal. calc. for $C_{78}H_{60}N_6$ (1081.37): C 86.64, H 5.59, N 7.77; found: C 86.70, H 5.77, N 7.60.

N,N-*Dihexyl-4-[(trimethylsilyl)ethynyl]aniline* (**20**). To a deoxygenated soln. of **14d** (1.5 g, 3.87 mmol) in $(i\text{-}Pr)_2NH$ (50 ml), **19** (1.27 ml, 0.86 g, 8.76 mmol), $[PdCl_2(PPh_3)_2]$ (80 mg, 0.11 mmol), and CuI (40 mg, 0.21 mmol) were added, and the mixture was stirred for 5 h at r.t. Hexane (50 ml) was added, and the mixture was filtered through a plug (SiO_2; CH_2Cl_2). The residue obtained after evaporation *in vacuo* was subjected to FC (SiO_2; hexane/CH_2Cl_2 5:1) to yield **20** (1.33 g, 95%). Colorless oil. IR (film): 2958, 2924, 2857, 2146, 1606, 1516, 1466, 1368, 1248, 1183, 864, 758, 632. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.21 (*s*, 9 H); 0.88 (*t*, $J = 6.5$, 6 H); 1.29

(*m*, 12 H); 1.53 (*m*, 4 H); 3.23 (*t*, *J* = 7.8, 4 H); 6.48 (*d*, *J* = 9.0, 2 H); 7.27 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 0.38; 14.12; 22.75; 26.85; 27.23; 31.77; 50.93; 90.95; 106.78; 108.53; 110.91; 133.11; 147.88. EI-MS: 357 (37, M^+), 286 (100, $[M - C_5H_{11}]^+$). Anal. calc. for $C_{23}H_{39}NSi$ (357.65): C 77.24, H 10.99, N 3.92; found: C 77.41, H 11.06, N 3.92.

4-Ethynyl-N,N-*dihexylaniline* (**21**). To **20** (1.25 g, 3.49 mmol) in THF (20 ml) and MeOH (20 ml), K_2CO_3 (0.96 g, 6.97 mmol) was added, and the mixture was stirred for 30 min at r.t. Hexane (50 ml) was added, and the mixture was filtered through a plug (SiO_2; AcOEt). Evaporation *in vacuo* gave **21** (0.98 g, 99%). Colorless oil. IR (film): 3305, 3092, 3042, 2926, 2851, 2100, 1608, 1517, 1466, 1369, 1292, 1255, 1180, 813, 642. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.90 (*t*, *J* = 6.8, 6 H); 1.31 (*m*, 12 H); 1.56 (*m*, 4 H); 2.94 (*s*, 1 H); 3.25 (*t*, *J* = 7.8, 4 H); 6.52 (*d*, *J* = 9.0, 2 H); 7.31 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.13; 22.76; 26.87; 27.22; 31.77; 50.97; 74.37; 85.06; 107.33; 110.94; 133.22; 148.05. EI-MS: 285 (20, M^+), 214 (100, $[M - C_5H_{11}]^+$). Anal. calc. for $C_{20}H_{31}N$ (285.47): C 84.15, H 10.95, N 4.91; found: C 83.97, H 10.79, N 4.86.

N,N-*Dihexyl-4-(3-{[4-(dihexylamino)phenyl]ethynyl}-6-(triisopropylsilyl)-4-[(triisopropylsilyl)ethynyl]-hex-3-ene-1,5-diyn-1-yl)benzenamine* (**18**). To a deoxygenated soln. of **22** [20a] (767 mg, 1.66 mmol) and **21** (946 mg, 3.32 mmol) in Et_3N (30 ml), $[PdCl_2(PPh_3)_2]$ (46 mg, 0.07 mmol) and CuI (23 mg, 0.12 mmol) were added, and the mixture was stirred for 16 h at r.t. Hexane (50 ml) was added, and the mixture was filtered through a plug (SiO_2; hexane/CH_2Cl_2 1:1). Evaporation *in vacuo* gave a brown oil that was subjected to FC (SiO_2; hexane/CH_2Cl_2 10:1) to yield **18** (1.00 g, 69%). Yellow oil. UV/VIS ($CHCl_3$): 312 (32900), 445 (58600). IR (film): 2928, 2863, 2196, 2170, 2134, 1603, 1520, 1465, 1407, 1363, 1248, 1186, 1110, 1019, 999, 862, 811. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.25 (*s*, 9 H); 0.90 (*t*, *J* = 6.8, 12 H); 1.13 (*s*, 21 H); 1.32 (*m*, 24 H); 1.57 (*m*, 8 H); 3.27 (*t*, *J* = 7.7, 8 H); 6.52 (*d*, *J* = 9.0, 2 H); 6.55 (*d*, *J* = 9.0, 2 H); 7.33 (*d*, *J* = 9.0, 2 H); 7.35 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 0.09; 11.55; 14.14; 18.81; 22.75; 26.86; 27.27; 31.76; 50.96; 86.39; 86.82; 99.90; 100.88; 100.93; 102.35; 103.00; 104.59; 108.20; 108.25; 110.90; 110.99; 111.80; 120.08; 133.28; 148.22; 148.26. MALDI-TOF-MS: 871 (100, M^+). Anal. calc. for $C_{58}H_{90}N_2Si_2$ (871.52): C 79.93, H 10.41, N 3.21; found: C 79.87, H 10.30, N 3.02.

4-((3Z)-4-{[4-(Dimethylamino)phenyl]ethynyl}-12-phenyl-10-(phenylethynyl)-3-{8-phenyl-6-(phenylethynyl)-5-[(triisopropylsilyl)ethynyl]oct-5-ene-1,3,7-triyn-1-yl}-9-[(triisopropylsilyl)ethynyl]dodeca-3,9-diene-1,5,7,11-tetrayn-1-yl)-N,N-*dimethylbenzenamine* (**17**). According to the protocol described for **5**/**6**, **15a** (70 mg, 0.10 mmol) was desilylated with Bu_4NF. Also, to a soln. of **23** [20a] (340 mg, 0.79 mmol) in THF (20 ml) and MeOH (10 ml), K_2CO_3 (213 mg, 1.55 mmol) was added, and the mixture was stirred for 2.5 h at r.t. After complete Me_3Si deprotection (TLC), CH_2Cl_2 (50 ml) was added, and the mixture was filtered through a plug (SiO_2; CH_2Cl_2). Evaporation *in vacuo* left a brown oil. Crude deprotected **15a** and **23** were dissolved in Me_2CO (150 ml), and *Hay* catalyst (10 ml) was added. The mixture was stirred for 1.5 h at r.t. exposed to air, filtered through a plug (SiO_2; acetone), and evaporated *in vacuo*. The residual brown oil was subjected to FC (hexane/AcOEt 4:1 → AcOEt) to yield **17** (70 mg, 57%). Reddish-brown solid. UV/VIS ($CHCl_3$): 302 (81500), 367 (57400), 460 (58400), 543 (sh, 31400). IR (KBr): 2936, 2857, 2162, 1603, 1521, 1441, 1363, 1161, 1108, 813, 754, 687. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.11 (*s*, 42 H); 23.01 (*s*, 12 H); 6.62 (*d*, *J* = 9.6, 4 H); 7.33–7.62 (*m*, 24 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.38; 18.76; 40.13; 82.51; 82.96; 83.86; 84.46; 86.63; 87.11; 87.33; 100.43; 100.68; 101.85; 103.11; 104.23; 108.68; 111.58; 115.43; 116.36; 121.16; 122.03; 122.30; 128.12; 128.40; 129.03; 129.23; 131.75; 132.04; 133.14; 150.55. FT-ICR-MALDI-MS: 1261 (27, $[M + K]^+$), 1245 (100, $[M + Na]^+$), 1222 (14, M^+). HR-FT-ICR-MALDI-MS: 1222.6003 (M^+, $C_{88}H_{82}N_2Si_2^+$; calc. 1222.6017). Anal. calc. for $C_{88}H_{82}N_2Si_2$ (1223.80): C 86.37, H 6.75, N 2.29; found: C 86.18, H 6.94, N 2.35.

4-((9Z)-18-[4-(Dihexylamino)phenyl]-3,16-bis[[4-(dihexylamino)phenyl]ethynyl}-9,10-bis{[4-(dimethylamino)phenyl]ethynyl}-4,15-bis[(triisopropylsilyl)ethynyl]octadeca-3,9,15-triene-1,5,7,11,13,17-hexayn-1-yl)-N,N-*dihexylbenzenamine* (**25**). To a soln. of **18** (387 mg, 0.44 mmol) in THF (20 ml) and MeOH (10 ml), K_2CO_3 (121 mg, 0.88 mmol) was added, and the mixture was stirred for 2.5 h at r.t. After complete Me_3Si deprotection, CH_2Cl_2 (50 ml) was added, and the mixture was filtered through a plug (SiO_2; CH_2Cl_2). Evaporation *in vacuo* left a brown oil that was taken up in Me_2CO (100 ml). To this was added a soln. of **15a** (50 mg, 0.074 mmol) that had been bis-silyl-deprotected with Bu_4NF as described for **5**/**6**, in Me_2CO (50 ml). *Hay* catalyst (10 ml) was added, and the mixture was stirred for 1 h at r.t. exposed to air. The soln. was filtered through a plug (SiO_2; Me_2CO), and evaporation *in vacuo* gave a solid that was purified by FC (SiO_2; hexane/CH_2Cl_2 3:1 → 1.5:1) to yield **25** (47 mg, 32%). Deep-purple waxy solid. UV/VIS ($CHCl_3$): 301 (96700), 486 (98800). IR (KBr): 2924, 2857, 2160, 1602, 1521, 1363, 1183, 1107, 812. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.81–0.92 (*m*, 24 H); 1.11 (*s*, 42 H); 1.23–1.31 (*m*, 48 H); 1.53 (*m*, 16 H); 2.99 (*s*, 12 H); 3.16–3.29 (*m*, 16 H); 6.50–6.62 (*m*, 12 H); 7.31–7.42 (*m*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.55; 14.15; 18.89; 22.77; 26.87; 27.3; 31.76; 40.17; 50.97; 82.17; 83.42; 83.66; 86.43; 87.03; 87.13; 87.74; 100.47; 102.87; 102.94; 103.82; 107.72; 108.16; 109.31; 109.81; 110.90; 111.30; 111.64;

115.92; 123.31; 133.12; 133.42; 133.70; 148.34; 148.52; 150.40 (35 out of 36 signals). FT-ICR-MALDI-MS: 1956 (39, M^+), 1799 (100, $[M - C_9H_{21}Si]^+$). Anal. calc. for $C_{136}H_{182}N_6Si_2$ (1957.11): C 83.46, H 9.37, N 4.29; found: C 83.43, H 9.50, N 4.44.

4-((3Z)-4-{[4-(Dimethylamino)phenyl]ethynyl}-12-(4-nitrophenyl)-10-[(4-nitrophenyl)ethynyl]-3-{8-(4-nitrophenyl)-6-[(4-nitrophenyl)ethynyl]-5-[(triisopropylsilyl)ethynyl]oct-5-ene-1,3,7-triyn-1-yl}-9-[(triisopropylsilyl)ethynyl]dodeca-3,9-diene-1,5,7,11-tetrayn-1-yl)-N,N-*dimethylbenzenamine* (**26**). TEE **15a** (90 mg, 0.13 mmol) was bis-deprotected with Bu_4NF as described for **5**/**6**. Also, Me_3Si deprotection of **24** [28] (417 mg, 0.8 mmol) with K_2CO_3 in THF/MeOH was performed as described for **17**. The two crude deprotected species were dissolved in Me_2CO (200 ml), and *Hay* catalyst (20 ml) was added. The mixture was stirred for 2 h at r.t. exposed to air, filtered through a plug (SiO_2; Me_2CO), and the solvents were evaporated *in vacuo* to yield a brown solid. FC (3 × hexane/AcOEt 4:1 → AcOEt) provided **26** (114 mg, 63%). Brown solid. UV/VIS ($CHCl_3$): 325 (87000), 400 (sh, 57600), 488 (49400), 594 (sh, 24800). IR (KBr): 2936, 2863, 2151, 1603, 1519, 1340, 1161, 853. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.09 (*s*, 42 H); 3.03 (*s*, 12 H); 6.64 (*d*, $J = 9.0$, 4 H); 7.42 (*d*, $J = 9.0$, 4 H); 7.65 (*d*, $J = 9.0$, 4 H); 7.68 (*d*, $J = 9.0$, 4 H); 8.21 (*d*, $J = 9.0$, 4 H); 8.22 (*d*, $J = 9.0$, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.33; 18.74; 40.16; 81.91; 83.85; 84.66; 85.50; 86.59; 90.47; 90.78; 98.03; 98.13; 101.09; 105.69; 106.33; 108.26; 111.64; 116.53; 118.60; 118.77; 123.51; 132.72; 128.44; 128.65; 132.46; 132.67; 133.22; 147.41; 147.49; 150.79. FT-ICR-MALDI-MS: 1425 (100, $[M + Na]^+$), 1402 (71, M^+). HR-FT-ICR-MALDI-MS: 1402.5430 (M^+, $C_{88}H_{78}N_6O_8Si_2^+$; calc. 1402.5420). Anal. calc. for $C_{88}H_{78}N_6O_8Si_2$ (1403.79): C 75.29, H 5.60, N 5.99; found: C 75.10, H 5.64, N 5.93.

4-[(9Z)-18-[4-(Dihexylamino)phenyl]-3,16-bis[[4-(dihexylamino)phenyl]ethynyl]-9,10-bis[(4-nitrophenyl)-ethynyl]-4,15-bis[(triisopropylsilyl)ethynyl]octadeca-3,9,15-triene-1,5,7,11,13,17-hexayn-1-yl}-N,N-*dihexylbenzenamine* (**27**). To a cooled (0°) soln. of **15b** (157 mg, 0.23 mmol) in moist THF (15 ml), Bu_4NF (0.69 ml of a 1M soln. in THF, 0.69 mmol) was added. After stirring for 10 min, TLC control indicated complete desilylation. The soln. was diluted with CH_2Cl_2 (50 ml) and filtered through a plug (SiO_2). The solvents were evaporated *in vacuo*, and the residue was dissolved in Me_2CO (100 ml). To this was added a soln. of **18** (1.266 g, 1.45 mmol) that had been Me_3Si-deprotected with K_2CO_3 in THF/MeOH as described for **17**, in Me_2CO (100 ml). *Hay* catalyst (10 ml) was added, and the mixture was stirred for 1.5 h at r.t. exposed to air. Filtration through a plug (SiO_2; Me_2CO), evaporation *in vacuo*, and FC (SiO_2; hexane/CH_2Cl_2 3:1 → 1:1) yielded **27** (145 mg, 32%). Brown solid. UV/VIS ($CHCl_3$): 311 (87400), 454 (80000). IR (KBr): 2925, 2859, 2158, 1601, 1521, 1341, 1186, 1108, 852, 812. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.83 (*t*, $J = 6.6$, 12 H); 0.89 (*t*, $J = 6.6$, 12 H); 1.12 (*s*, 42 H); 1.23 (*m*, 24 H); 1.31 (*m*, 24 H); 1.53 (*m*, 16 H); 3.20 (*t*, $J = 7.8$, 8 H); 3.27 (*t*, $J = 7.7$, 8 H); 6.52 (*d*, $J = 9.1$, 4 H); 6.53 (*d*, $J = 9.1$, 4 H); 7.35 (*t*, $J = 9.1$, 8 H); 7.63 (*d*, $J = 8.9$, 4 H); 8.21 (*d*, $J = 8.9$, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.39; 14.02; 18.75; 22.64; 26.75; 27.14; 31.65; 50.91; 81.41; 81.98; 87.20; 87.44; 87.88; 89.15; 91.45; 97.91; 101.03; 102.46; 104.35; 104.49; 107.54; 107.80; 108.75; 110.94; 111.26; 117.63; 123.80; 124.66; 128.80; 132.44; 133.67; 133.83; 147.59; 148.65; 148.71. FT-ICR-MALDI-MS: 1999 (49, $[M + K]^+$), 1983 (92, $[M + Na]^+$), 1960 (49, M^+), 1803 (100, $[M - Si(CH(CH_3)_2)_3]^+$). HR-FT-ICR-MALDI-MS: 1960.2829 (M^+, $^{13}C^{12}C_{131}H_{170}N_6O_4Si_2^+$; calc. 1960.2822). Anal. calc. for $C_{132}H_{170}N_6O_4Si_2$ (1960.97): C 80.85, H 8.74, N 4.29; found: C 81.02, H 6.68, N 4.26.

*4,4′-({7,12-Bis[3-phenyl-1-(phenylethynyl)prop-2-yn-1-ylidene]cyclohexadec-1-ene-3,5,8,10,13,15-hexayne-1,2-diyl}bis(ethyne-2,1-diyl))bis[*N,N-*dimethylaniline]* (**7**). To a cooled (0°) soln. of **17** (62 mg, 0.05 mmol) in moist THF (10 ml), Bu_4NF (0.15 ml of a 1.0M soln. in THF, 0.15 mmol) was added dropwise. After stirring for 10 min, TLC control indicated complete desilylation. CH_2Cl_2 (20 ml) was added, and the soln. was filtered through a plug (SiO_2; CH_2Cl_2). The solvents were evaporated *in vacuo*, and the residue was dissolved in Me_2CO (150 ml). *Hay* catalyst (5 ml) was added, and the mixture was stirred for 1 h at r.t. exposed to air. After filtration through a plug (SiO_2), the solvent was evaporated *in vacuo*, and the residue was subjected to FC (SiO_2; hexane/CH_2Cl_2 2:1 → 1:2) to yield **7** (22 mg, 48%). Dark-brown solid. UV/VIS ($CHCl_3$): 312 (67500), 381 (28500), 494 (103900), 588 (sh, 31900). IR (KBr): 2146, 1600, 1522, 1362, 1180, 1085, 808, 752, 685. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.01 (*s*, 12 H); 6.62 (*d*, $J = 9.3$, 4 H); 7.35–7.42 (*m*, 16 H); 7.54–7.60 (*m*, 8 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 40.09; 82.67; 86.06; 86.87; 86.93; 86.94; 87.18; 87.37; 88.19; 96.63; 101.01; 101.32; 105.15; 108.75; 111.70; 113.67; 116.08; 117.78; 121.94; 128.44; 129.57; 132.16; 132.29; 133.29; 150.80 (25 out of 28 signals). FT-ICR-MALDI-MS: 908 (100, M^+). HR-FT-ICR-MALDI-MS: 908.3180 (M^+, $C_{70}H_{40}N_2^+$; calc. 908.3191). Anal. calc. for $C_{70}H_{40}N_2$ (909.10): C 92.48, H 4.43, N 3.08; found: C 92.37, H 4.49, N 3.04.

*4,4′,4″,4‴-[(11,12-Bis{[4-(dimethylamino)phenyl]ethynyl}cyclohexadec-11-ene-2,4,7,9,13,15-hexayne-1,6-diylidene)bis(penta-1,4-diyne-1,5-diyl-3-ylidene)]tetrakis[*N,N-*dihexylaniline]* (**8**). To a cooled (0°) soln. of **25** (45 mg, 0.023 mmol) in moist THF (15 ml), Bu_4NF (0.07 ml of a 1.0M soln. in THF, 0.07 mmol) was added dropwise. After stirring for 10 min, CH_2Cl_2 (50 ml) was added, and the soln. was filtered through a plug (SiO_2; CH_2Cl_2). The residue obtained by evaporation *in vacuo* was dissolved in Me_2CO (150 ml), and *Hay* catalyst

(10 ml) was added. After stirring for 1 h at r.t. exposed to air, the soln. was filtered through a plug (SiO_2). Evaporation *in vacuo* and FC (SiO_2; hexane/CH_2Cl_2 2:1 → 1:2) afforded **8** (11.9 mg, 32%). Deep-purple waxy solid. UV/VIS ($CHCl_3$): 304 (82400), 521 (106100), 614 (99900). IR ($CHCl_3$): 2957, 2930, 2858, 2164, 1603, 1522, 1366, 1189, 1086, 986, 817. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.88–0.89 (*m*, 24 H); 1.26–1.54 (*m*, 48 H); 1.57 (*m*, 16 H); 3.00 (*s*, 12 H); 3.26 (*m*, 16 H); 6.53–6.62 (*m*, 12 H); 7.37–7.42 (*m*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.18; 22.78; 26.87; 27.28; 31.76; 40.17; 51.02; 83.58; 84.85; 86.00; 86.05; 86.51; 87.24; 87.33; 89.79; 96.85; 103.58; 103.71; 104.00; 107.50; 109.10; 110.41; 111.07; 111.59; 115.26; 117.36; 133.06; 133.72; 133.85; 148.57; 146.61; 150.44 (32 out of 34 signals). FT-ICR-MALDI-MS: 1681 (2, $[M+K]^+$), 1665 (12, $[M+Na]^+$), 1642 (100, M^+). HR-FT-ICR-MALDI-MS: 1642.1141 (M^+, $^{13}C^{12}C_{117}H_{140}N_6^+$; calc. 1642.1139).

*4,4′-[(7,12-Bis{3-(4-nitrophenyl)-1-[(4-nitrophenyl)ethynyl]prop-2-yn-1-ylidene}cyclohexadec-1-ene-3,5,8,10,13,15-hexayne-1,2-diyl)bis(ethyne-2,1-diyl)]bis[*N,N*-dimethylaniline]* (**28**). Starting from **26** and according to the protocol described for the synthesis of **8**, traces of unstable **28** were isolated. FT-ICR-MALDI-MS: 1088 (100, M^+). HR-FT-ICR-MALDI-MS: 1088.2639 (M^+, $C_{70}H_{36}N_6O_8^+$; calc. 1088.2595).

*4,4′,4″,4‴-[{11,12-Bis[(4-nitrophenyl)ethynyl]cyclohexadec-11-ene-2,4,7,9,13,15-hexayne-1,6-diylidene}bis(penta-1,4-diyne-1,5-diyl-3-ylidene)]tetrakis[*N,N*-dihexylaniline]* (**9**). To a cooled (0°) soln. of **27** (145 mg, 0.074 mmol) in moist THF (15 ml), Bu_4NF (0.22 ml of a 1.0M soln. in THF, 0.22 mmol) was added dropwise. After stirring for 10 min, CH_2Cl_2 (50 ml) was added, and the soln. was filtered through a plug (SiO_2; CH_2Cl_2). The residue obtained by evaporation *in vacuo* was dissolved in Me_2CO (200 ml), and *Hay* catalyst (10 ml) was added. After stirring for 1.5 h at r.t. exposed to air, the soln. was filtered through a plug (SiO_2; Me_2CO). Evaporation *in vacuo* and FC (SiO_2; hexane/CH_2Cl_2 3:1 → 1:1) gave **9** (16.6 mg, 14%). Deep-purple waxy solid. UV/VIS ($CHCl_3$): 303 (85500), 542 (98800), 614 (89300). IR ($CHCl_3$): 2957, 2930, 2858, 2156, 1601, 1522, 1349, 1187, 1130, 854, 817. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.87 (*t*, *J* = 6.8, 24 H); 1.30 (*m*, 48 H); 1.57 (*m*, 16 H); 3.27 (*t*, *J* = 7.5, 16 H); 6.55 (*d*, *J* = 8.4, 8 H); 7.38 (*d*, *J* = 8.7, 8 H); 7.65 (*d*, *J* = 9.0, 4 H); 8.20 (*d*, *J* = 9.0, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.03; 22.67; 26.78; 27.22; 29.71; 31.68; 51.01; 84.02; 84.52; 86.66; 86.95; 87.58; 87.70; 90.50; 92.11; 96.52; 98.59; 104.54; 105.47; 107.32; 107.37; 109.44; 111.21; 111.24; 116.91; 119.12; 123.83; 128.35; 128.81; 132.44; 134.02; 147.71; 149.017; 149.022. FT-ICR-MALDI-MS: 1646 (100, M^+). HR-FT-ICR-MALDI-MS: 1644.9992 (M^+, $C_{114}H_{128}N_6^+$; calc. 1644.9997).

Triisopropyl(17-phenyl-15-(phenylethynyl)-3-[3-phenyl-1-(phenylethynyl)prop-2-yn-1-ylidene]-8,9-bis{8-phenyl-6-(phenylethynyl)-5-[(triisopropylsilyl)ethynyl]oct-5-ene-1,3,7-triyn-1-yl}-14-[(triisopropylsilyl)ethynyl]heptadeca-8,14-diene-1,4,6,10,12,16-hexayn-1-yl)silane (**31**). To a soln. of tetrakis(trimethylsilyl)-protected **29** [20a] (65 mg, 0.16 mmol) in THF/MeOH (1:1, 20 ml), K_2CO_3 (50 mg, 0.36 mmol) was added, and the mixture was stirred for 30 min at r.t. Me_2CO (50 ml) was added, and the mixture was filtered through a plug (SiO_2; Me_2CO). A soln. of Me_3Si-deprotected **23** (for the deprotection protocol, see synthesis of **17**) [20a] (957 mg, 1.90 mmol) in Me_2CO (200 ml) was added, followed by *Hay* catalyst (15 ml). The mixture was stirred for 2.5 h at r.t. exposed to air, then filtered through a plug (SiO_2; Me_2CO), and evaporated *in vacuo*. FC (SiO_2; hexane/AcOEt 5:1) gave **31** (114 mg, 39%). Red waxy solid. UV/VIS ($CHCl_3$): 289 (101000), 373 (101000), 444 (sh, 60800), 505 (44500). IR ($CHCl_3$): 2944, 2866, 2186, 1492, 1463, 1443, 1070, 998, 883. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.10 (*s*, 84 H); 7.33–7.37 (*m*, 24 H); 7.49–7.56 (*m*, 16 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.38; 18.76; 81.83; 82.02; 86.37; 86.98; 87.07; 87.21; 101.16; 101.21; 101.44; 103.72; 114.82; 119.02; 121.83; 122.16; 122.22; 128.17; 128.44; 129.20; 129.48; 131.81; 132.01. MALDI-TOF-MS: 1846 (100, M^+).

*4-(18-[4-(Dihexylamino)phenyl]-9,10-bis{8-[4-(dihexylamino)phenyl]-6-{[4-(dihexylamino)phenyl]ethynyl}-5-[(triisopropylsilyl)ethynyl]oct-5-ene-1,3,7-triyn-1-yl}-3,16-bis{[4-(dihexylamino)phenyl]ethynyl}-4,15-bis[(triisopropylsilyl)ethynyl]octadeca-3,9,15-triene-1,5,7,11,13,17-hexayn-1-yl)-*N,N*-dihexylbenzenamine* (**32**). To a soln. of tetrakis(trimethylsilyl)-protected **29** [20a] (35 mg, 0.085 mmol) in THF/MeOH 1:1 (20 ml), K_2CO_3 (44 mg, 0.32 mmol) was added and the mixture was stirred for 15 min at r.t. Me_2CO (50 ml) was added, and the mixture was filtered through a plug (SiO_2; Me_2CO). A soln. of **18** (1.486 g, 1.70 mmol), which had been Me_3Si-deprotected as described for the preparation of **25**, in Me_2CO (150 ml) was added, followed by *Hay* catalyst (15 ml). The mixture was stirred for 2.5 h at r.t. exposed to air, then filtered through a plug (SiO_2; Me_2CO), and evaporated *in vacuo*. FC (short SiO_2 column; hexane/AcOEt 10:1), followed by gravity GPC (*Bio-Beads 1-SX*; THF), afforded **32** (109 mg, 39%). Brown waxy solid. UV/VIS ($CHCl_3$): 304 (147800), 459 (143400), 641 (sh, 43800). IR ($CHCl_3$): 2943, 2931, 2863, 2161, 1601, 1521, 1368, 1110, 816. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.83 (*t*, *J* = 6.6, 24 H); 0.90 (*t*, *J* = 6.6, 24 H); 1.10 (*s*, 84 H); 1.23 (*m*, 48 H); 1.31 (*s*, 48 H); 1.54 (*m*, 32 H); 3.25 (*m*, 32 H); 6.50 (*d*, *J* = 8.9, 8 H); 6.52 (*d*, *J* = 8.9, 8 H); 7.26 (*d*, *J* = 8.9, 8 H); 7.33 (*d*, *J* = 8.9, 8 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.39; 14.03; 14.08; 18.76; 22.65; 22.71; 26.76; 26.81; 27.16; 27.28; 31.67; 31.72; 50.92; 82.03; 82.70; 86.77; 87.36; 88.01; 88.99; 100.67; 102.56; 103.52; 105.14; 107.27; 108.13; 109.11; 110.93; 111.30; 117.48; 124.35; 133.60; 133.78; 148.52; 148.78. MALDI-TOF-MS: 3312 (100, M^+).

*(17-[3,5-Di-(*tert*-butyl)phenyl]-3-(3-[3,5-di-(*tert*-butyl)phenyl]-1-{[3,5-di-(*tert*-butyl)phenyl]ethynyl}-prop-2-yn-1-ylidene)-8,9-bis(8-[3,5-di-(*tert*-butyl)phenyl]-6-{[3,5-di-(*tert*-butyl)phenyl]ethynyl}-5-[(triisopropylsilyl)ethynyl]oct-5-ene-1,3,7-triyn-1-yl)-15-{[3,5-di-(*tert*-butyl)phenyl]ethynyl}-14-[(triisopropylsilyl)ethynyl]-heptadeca-8,14-diene-1,4,6,10,12,16-hexayn-1-yl)(triisopropyl)silane* (**33**). To a soln. of tetrakis(trimethylsilyl)-protected **29** [20a] (50 mg, 0.11 mmol) in THF/MeOH (1:1, 20 ml), K_2CO_3 (38 mg, 0.27 mmol) was added and the mixture was stirred for 30 min at r.t. Me_2CO (50 ml) was added, and the mixture was filtered through a plug (SiO_2; Me_2CO). A soln. of Me_3Si-deprotected (for the deprotection protocol, see [16b] or the preparation of **17**) **30** (953 mg, 1.31 mmol) in Me_2CO (150 ml) was added, followed by *Hay* catalyst (15 ml). The mixture was stirred for 1.5 h at r.t. exposed to air, then filtered through a plug (SiO_2; Me_2CO), and evaporated *in vacuo*. FC (hexane/CH_2Cl_2 98:2 → 90:10) afforded **33** (65 mg, 29%). Red solid. UV/VIS ($CHCl_3$): 255 (107900), 276 (98742), 375 (97700), 413 (sh, 73900), 504 (sh, 36700). IR ($CHCl_3$): 2965, 2866, 2186, 1588, 1464, 1364, 1248, 1141, 879. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.07 (*s*, 84 H); 1.28 (*s*, 72 H); 1.30 (*s*, 72 H); 7.34 (*d*, J = 1.8, 8 H); 7.40 (*m*, 16 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.32; 18.67; 31.31; 34.78; 34.84; 81.29; 81.77; 85.97; 86.32; 86.64; 86.67; 101.93; 102.16; 102.50; 103.39; 114.50; 119.26; 121.23; 121.48; 122.36; 123.75; 124.02; 126.21; 126.52; 150.80; 151.06. MALDI-TOF-MS: 2750 (100, M^+).

*4-{5-[4-(Dihexylamino)phenyl]-3-[10,19,24-tris(3-[4-(dihexylamino)phenyl]-1-{2-[4-(dihexylamino)phenyl]ethynyl}prop-2-yn-1-ylidene)-1,2,3,4,6,7,8,9,11,12,13,14,15,16,17,18,20,21,22,23,25,26,27,28-tetracosadehydro-19,24-dihydrocyclohexadeca[*a*]cyclohexadecen-5(10*H*)-ylidene]penta-1,4-diyn-1-yl}-*N,N*-dihexylaniline* (**10**). To a cooled (0°) soln. of **32** (37.9 mg, 0.011 mmol) in moist THF (20 ml), Bu_4NF (0.1 ml of a 1.0M soln. in THF, 0.1 mmol) was added. After stirring for 10 min, TLC control indicated complete desilylation. CH_2Cl_2 (30 ml) was added, and the soln. was filtered through a plug (SiO_2; CH_2Cl_2). Evaporation *in vacuo* left a brown oil that was redissolved in a mixture of THF, Me_2CO, and PhH (150 ml, 1:1:1). *Hay* catalyst (15 ml) was added, and the mixture was stirred for 2 h at r.t. exposed to air. The deep-purple soln. was filtered through a plug (SiO_2; Me_2CO) and evaporated *in vacuo*. FC (hexane/CH_2Cl_2 4:1 → 1:1) gave **10** (4.6 mg, 16%). Deep-purple waxy solid. UV/VIS ($CHCl_3$): 306 (122600), 558 (176700), 591 (sh, 160200), 698 (85900). IR ($CHCl_3$): 2957, 2930, 2858, 2159, 1601, 1522, 1265, 1188, 1129, 1085, 909. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86 (*m*, 48 H); 1.23 (*m*, 48 H); 1.29 (*m*, 48 H); 1.51 (*m*, 32 H); 3.18 (*t*, J = 8.0, 16 H); 3.26 (*t*, J = 7.8, 16 H); 6.53 (*t*, J = 9.2, 16 H); 7.38 (*d*, J = 9.2, 8 H); 7.39 (*d*, J = 9.2, 8 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.04; 22.670; 22.673; 26.75; 26.79; 27.22; 27.23; 31.64; 31.68; 50.98; 51.00; 84.32; 84.33; 86.69; 87.42; 87.56; 87.86; 92.27; 96.79; 104.65; 104.84; 107.55; 107.57; 109.76; 111.21; 111.22; 116.38; 120.22; 133.95; 134.13; 148.90; 148.94. MALDI-TOF-MS: 2683.7 (100, M^+).

*5,10,19,24-Tetrakis(3-[3,5-di(*tert*-butyl)phenyl]-1-{2-[3,5-di(*tert*-butyl)phenyl]ethynyl}prop-2-yn-1-ylidene)-1,2,3,4,6,7,8,9,11,12,13,14,15,16,17,18,20,21,22,23,25,26,27,28-tetracosadehydro-5,10,19,24-tetrahydrocyclohexadeca[*a*]cyclohexadecene* (**11**). To a cooled (0°) soln. of **33** (90 mg, 0.0328 mmol) in moist THF (20 ml), Bu_4NF (0.5 ml of a 1.0M soln. in THF, 0.5 mmol) was added. After stirring for 10 min, TLC control indicated complete desilylation. CH_2Cl_2 (100 ml) was added, and the soln. was filtered through a plug (SiO_2; CH_2Cl_2). Evaporation *in vacuo* left a red oil that was redissolved in a mixture of THF, Me_2CO, and PhH (450 ml, 1:1:1). *Hay* catalyst (25 ml) was added, and the mixture was stirred for 1 h at r.t. exposed to air. The deep-purple soln. was filtered through a plug (SiO_2; Me_2CO) and evaporated *in vacuo*. The residue was subjected to FC (SiO_2; hexane/AcOEt 20:1) to provide **11** (61.5 mg, 88%). Brown solid. UV/VIS ($CHCl_3$): 408 (65400), 498 (122500), 595 (42300). IR ($CHCl_3$): 3023, 2966, 2905, 2870, 2181, 1589, 1477, 1431.77, 1395, 1364, 1248, 879. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.25 (*s*, 72 H); 1.29 (*s*, 72 H); 7.36 (*d*, J = 2.0, 16 H); 7.43 (*t*, J = 2.0, 8 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 31.29; 31.31; 34.82; 34.86; 84.14; 85.27; 86.01; 86.08; 87.03; 87.52; 90.85; 96.27; 103.25; 103.93; 114.61; 115.79; 120.82; 120.89; 121.47; 124.20; 124.37; 126.37; 126.42; 151.05; 151.06. MALDI-TOF-MS: 2115 (100, M^+). FT-ICR-MALDI-MS: 2114 (100, M^+). HR-FT-ICR-MALDI-MS: 2113.3166 (M^+, $C_{162}H_{168}^+$; calc. 2113.3146).

REFERENCES

[1] F. Sondheimer, *Acc. Chem. Res.* **1972**, *5*, 81.

[2] M. Nakagawa, *Angew. Chem.* **1979**, *91*, 215; *Angew. Chem., Int. Ed.* **1979**, *18*, 202; H. A. Staab, J. Ipaktschi, A. Nissen, *Chem. Ber.* **1971**, *104*, 1182.

[3] a) Y. Li, Y. Rubin, F. Diederich, K. N. Houk, *J. Am. Chem. Soc.* **1990**, *112*, 1618; b) F. Diederich, Y. Rubin, O. L. Chapman, N. S. Goroff, *Helv. Chim. Acta* **1994**, *77*, 1441.

[4] a) M. J. Cook, M. J. Heeney, *Chem. – Eur. J.* **2000**, *6*, 3958; b) E. M. Garcia-Frutos, F. Fernandez-Lazaro, E. M. Maya, P. Vazquez, T. Torres, *J. Org. Chem.* **2000**, *65*, 6841; c) G. J. Palmer, S. R. Parkin, J. E. Anthony,

Angew. Chem. **2001**, *113*, 2577; *Angew. Chem., Int. Ed.* **2001**, *40*, 2509; d) M. Laskoski, M. D. Smith, J. G. M. Morton, U. H. F. Bunz, *J. Org. Chem.* **2001**, *66*, 5174; e) T. Nishinaga, N. Nodera, Y. Miyata, K. Komatsu, *J. Org. Chem.* **2002**, *67*, 6091; f) A. J. Boydston, M. M. Haley, R. V. Williams, J. R. Armantrout, *J. Org. Chem.* **2002**, *67*, 8812; g) J. A. Marsden, G. J. Palmer, M. M. Haley, *Eur. J. Org. Chem.* **2003**, 2355.

[5] R. R. Tykwinski, *Chem. Commun.* **1999**, 905; S. Eisler, R. R. Tykwinski, *Angew. Chem.,* **1999**, *111*, 2138; *Angew. Chem., Int. Ed.* **1999**, *38*, 1940; K. Campbell, R. McDonald, N. R. Branda, R. R. Tykwinski, *Org. Lett.* **2001**, *3*, 1045.

[6] Y. Tobe, N. Utsumi, K. Kawabata, A. Nagano, K. Adachi, S. Araki, M. Sonoda, K. Hirose, K. Naemura, *J. Am. Chem. Soc.* **2002**, *124*, 5350.

[7] C.-H. Lin, J. Tour, *J. Org. Chem.* **2002**, *67*, 7761.

[8] D. Zhao, J. S. Moore, *Chem. Commun.* **2003**, 807.

[9] S. Höger, K. Bonrad, A. Mourran, U. Beginn, M. Möller, *J. Am. Chem. Soc.* **2001**, *123*, 5651.

[10] M. Mayor, C. Didschies, *Angew. Chem.* **2003**, *115*, 3284; *Angew. Chem., Int. Ed.* **2003**, *42*, 3176.

[11] C. Grave, A. D. Schlüter, *Eur. J. Org. Chem.* **2002**, 3075.

[12] T. Kawase, Y. Seirai, H. R. Darabi, M. Oda, Y. Sarakai, K. Tashiro, *Angew. Chem.* **2003**, *115*, 1659; *Angew. Chem., Int. Ed.* **2003**, *42*, 1621.

[13] M. Laskoski, W. Steffen, J. G. M. Morton, M. D. Smith, U. H. F. Bunz, *J. Am. Chem. Soc.* **2002**, *124*, 13814.

[14] A. de Meijere, S. I. Kozhushkov, T. Haumann, R. Boese, C. Puls, M. J. Cooney, L. T. Scott, *Chem. – Eur. J.* **1995**, *1*, 124; A. de Meijere, S. I. Kozhushkov, *Top. Curr. Chem.* **1999**, *201*, 1; A. de Meijere, S. I. Kozhushkov, *Chem. – Eur. J.* **2002**, *8*, 3195.

[15] M. Laskoski, W. Steffen, M. D. Smith, U. H. F. Bunz, *Chem. Commun.* **2001**, 691; M. Laskoski, M. D. Smith, J. G. M. Morton, U. H. F. Bunz, *J. Org. Chem.* **2001**, *66*, 5174; J. Jusélius, D. Sundholm, *Phys. Chem. Chem. Phys.* **2001**, *3*, 2433.

[16] a) M. Schreiber, R. R. Tykwinski, F. Diederich, R. Spreiter, U. Gubler, C. Bosshard, I. Poberjai, P. Günter, C. Boudon, J.-P. Gisselbrecht, M. Gross, U. Jonas, H. Ringsdorf, *Adv. Mater.* **1997**, *9*, 339; b) 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.

[17] F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, *104*, 1123; *Angew. Chem., Int. Ed.* **1992**, *31*, 1101; F. Diederich, *Nature* **1994**, *369*, 199; Y. Rubin, F. Diederich, in 'Stimulating Concepts in Chemistry', Eds. J. F. Stoddart, F. Vögtle, M. Shibasaki, Wiley-VCH, Weinheim, 2000, pp. 163 – 186.

[18] W. B. Wan, M. M. Haley, *J. Org. Chem.* **2001**, *66*, 3893; U. H. F. Bunz, Y. Rubin, Y. Tobe, *Chem. Soc. Rev.* **1999**, *28*, 107.

[19] F. Diederich, Y. Rubin, C. B. Knobler, R. L. Whetten, K. E. Schriver, K. N. Houk, Y. Li, *Science* **1989**, *245*, 1088; S. W. McElvany, M. M. Ross, N. S. Goroff, F. Diederich, *Science* **1993**, *259*, 1594.

[20] a) J. Anthony, A. M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C. B. Knobler, P. Seiler, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 13; b) R. R. Tykwinski, F. Diederich, *Liebigs Ann. Chem. Recl. Trav. Chim. Pays-Bas* **1997**, 649; c) F. Diederich, *Chem. Commun.* **2001**, 219.

[21] a) J. Anthony, C. B. Knobler, F. Diederich, *Angew. Chem.* **1993**, *105*, 437; *Angew. Chem., Int. Ed.* **1993**, *32*, 406; b) 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.

[22] A. M. Boldi, F. Diederich, *Angew. Chem.* **1994**, *106*, 482; *Angew. Chem., Int. Ed.* **1994**, *33*, 468.

[23] C. Boudon, J.-P. Gisselbrecht, M. Gross, J. Anthony, A. M. Boldi, R. Faust, T. Lange, D. Philp, J.-D. van Loon, F. Diederich, *J. Electroanal. Chem.* **1995**, *394*, 187.

[24] C. Lepetit, M. B. Nielsen, F. Diederich, R. Chauvin, *Chem. – Eur. J.* **2003**, *9*, 5056.

[25] P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem.* **2000**, *112*, 2740; *Angew. Chem., Int. Ed.* **2000**, *39*, 2632.

[26] F. Mitzel, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Diederich, *Chem. Commun.* **2002**, 2318.

[27] F. Mitzel, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Commun.* **2003**, 1634.

[28] R. R. Tykwinski, M. Schreiber, R. P. Carlon, F. Diederich, V. Gramlich, *Helv. Chim. Acta* **1996**, *79*, 2249.

[29] R. E. Martin, J. Bartek, F. Diederich, R. R. Tykwinski, E. C. Meister, A. Hilger, H. P. Lüthi, *J. Chem. Soc., Perkin Trans 2* **1998**, 233.

[30] A. Hilger, J.-P. Gisselbrecht, R. R. Tykwinski, C. Boudon, M. Schreiber, R. E. Martin, H. P. Lüthi, M. Gross, F. Diederich, *J. Am. Chem. Soc.* **1997**, *119*, 2069; C. Dehu, F. Meyers, J. L. Brédas, *J. Am. Chem. Soc.* **1993**, *115*, 6198.

[31] N. N. P. Moonen, R. Gist, C. Boudon, J.-P. Gisselbrecht, P. Seiler, T. Kawai, A. Kishioka, M. Gross, M. Irie, F. Diederich, *Org. Biomol. Chem.* **2003**, *1*, 2032.

[32] R. R. Tykwinski, U. Gubler, R. E. Martin, F. Diederich, C. Bosshard, P. Günter, *J. Phys. Chem., B* **1998**, *102*, 4451.
[33] D. Dubois, G. Moninot, W. Kutner, M. T. Jones, K. M. Kadish, *J. Phys. Chem.* **1992**, *96*, 7137; L. Echegoyen, F. Diederich, L. E. Echegoyen, in 'Fullerenes: Chemistry, Physics, and Technology', Eds. K. M. Kadish, R. S. Ruoff, Wiley, New York, 2000, pp 1 – 51.
[34] J. J. La Clair, *J. Am. Chem. Soc.* **1997**, *119*, 7676.

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