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Two-Dimensional Acetylenic Scaffolding: Extended Donor-Substituted Perethynylated Dehydroannulenes

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Abstract: Starting from (*Z*)-bis(*N*,*N*-diisopropylanilino)-substituted tetraethynylethene (TEE), perethynylated octadehydro[12]- and dodecadehydro[18]annulenes were prepared by oxidative Hay coupling. The dodecadehydro[18]annulene with six peripheral *N*,*N*-diisopropylanilino substituents was characterized by X-ray crystallography. Elongation of the *Z*-bisdeprotected TEE by Cadiot–Chodkiewicz coupling with 1-bromo-2-(triisopropylsilyl)ethyne provided a *Z*-configured bis(butadiyne), which after alkyne deprotection afforded under Hay coupling conditions *N*,*N*-diisopropylanilino-substituted perethynylated hexadecadehydro[20]- and tetracosadehydro[30]annulenes. The diisopropylanilino substituents enhance the properties of these unprecedented all-carbon perimeters in several distinct ways. They ensure their solubility, increase their stability, and importantly, engage in strong intramolecular charge-transfer interactions with the electron-accepting all-carbon cores, resulting in intense, bathochromically shifted charge-transfer bands in the UV/Vis spectra. The charge-transfer character of these bands was confirmed by protonation-neutralization experiments. The redox properties of the new carbon-rich chromophores were investigated by cyclic voltammetry and rotating disk voltammetry, which indicated different redox behavior for aromatic ($4n+2$ π electrons) and antiaromatic ($4n$ π electrons) dehydroannulenes.

Keywords: alkynes · charge transfer · conjugation · dehydroannulenes · electrochemistry

Introduction

Acetylenic macrocycles are the subject of intensive research at the interface between synthetic and physical organic chemistry as well as advanced materials science.[1,2] In particular, carbon-rich structures such as dehydroannulenes[3–5] and dehydrobenzoannulenes (DBAs)[6,7] have attracted much attention for several reasons. They are studied both experimentally and theoretically to enhance further the understanding of aromaticity/antiaromaticity and, in general, π conjugation in unsaturated macrocyclic systems.[8] With their extended π chromophores, a number of representatives feature interesting optoelectronic properties such as high third-order optical nonlinearities.[2d,9] Furthermore, some of these acetylenic macrocycles represent hypothetical constituents of two-dimensional all-carbon networks such as graphyne or graphdiyne, which are predicted to display fascinating electronic and mechanical properties.[1b,10–12] Also, some of them act as potent receptors for compounds such as fullerenes.[2h]

Over the past decade, we developed a large library of tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne) building blocks[1c,g] and applied them to the construction of novel families of acetylenic macrocycles such as perethynylated dehydroannulenes,[13] expanded radialenes,[2d,9a,13b,14] and radiaannulenes.[13d,15] With their numerous sp-hybridized carbon atoms, the all-carbon cores of these systems feature potent electron-accepting properties. Among the first derivatives prepared were the per(silylethynylated) octadehydro[12]annulene **1a**, with an antiaromatic macrocyclic perimeter as revealed by UV/Vis and ^{1}H NMR spectroscopy, and the larger, aromatic dodecadehydro[18]annulene **2a**.[13a,b] Later, the terminally *N*,*N*-dimethylanilino-substituted derivatives **1b** and **2b** were synthesized,[13c,d] as well as a

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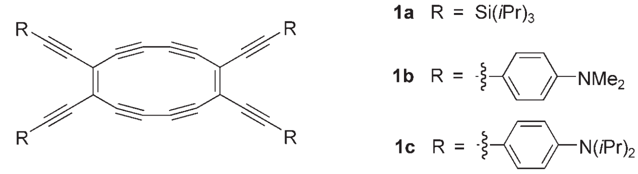

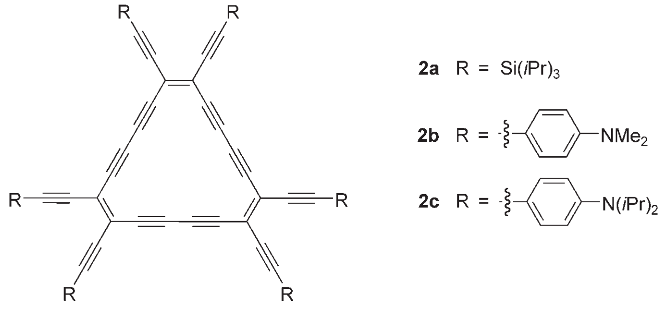

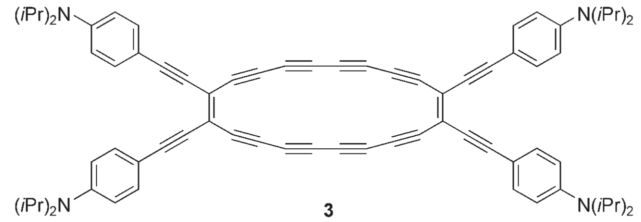

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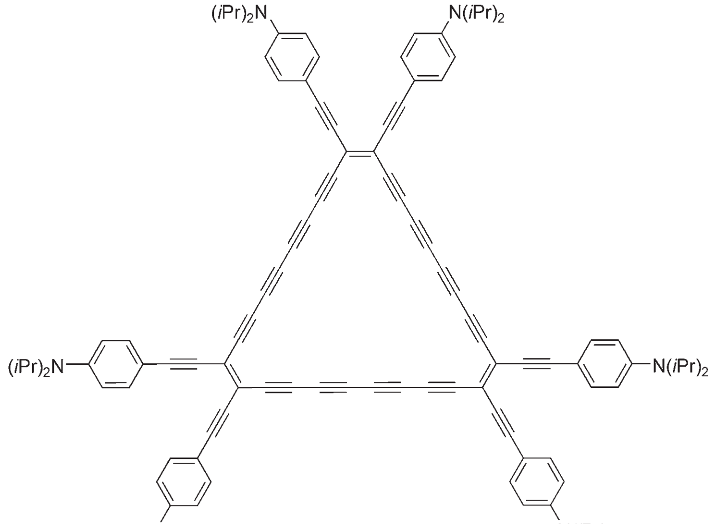

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series of anilino-substituted expanded radialenes[2d,9a] and radiaannulenes.[13d,15] The combined investigation of all three classes of acetylenic macrocycles clearly demonstrated three beneficial effects obtained upon introduction of the peripheral π-electron donor groups: 1) the solubility of the compounds is enhanced, 2) the electron-deficient all-carbon cores are stabilized against nucleophilic attack and cycloadditions, and 3) intense bathochromically shifted charge-transfer (CT) bands result from strong intramolecular CT interactions between these groups and the electron-accepting all-carbon cores.[13d]

In view of the appealing optoelectronic properties of donor-substituted **2a** and **2b**, we became interested in the preparation of even larger derivatives. Herein, we describe the synthesis and properties of the extended donor-substituted hexadecadehydro[20]annulene **3** and tetracosadehydro[30]annulene **4**. To enhance further the solubility and stability of these extended unsaturated π chromophores and their TEE precursors, we replaced the *N,N*-dimethylanilino with *N,N*-diisopropylanilino residues as peripheral electron-donating groups. For comparison, the *N,N*-diisopropylanilino-substituted [12]- and [18]annulenes **1c** and **2c** were also prepared.

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François Diederich *was born in 1952 in Luxembourg and received his PhD from the Univ. of Heidelberg in 1979 for work on the synthesis of kekulene with Prof. Heinz A. Staab. After postdoctoral studies at the Univ. of California, Los Angeles, he had his habilitation at the Max-Planck-Institut für Medizinische Forschung (1981–1985). Subsequently, he joined the Department of Chemistry and Biochemistry at UCLA, where he became Full Prof. of Organic and Bioorganic Chemistry in 1989. He returned to Europe in 1992 to the Department of Chemistry and Applied Biosciences at ETH Zürich.*

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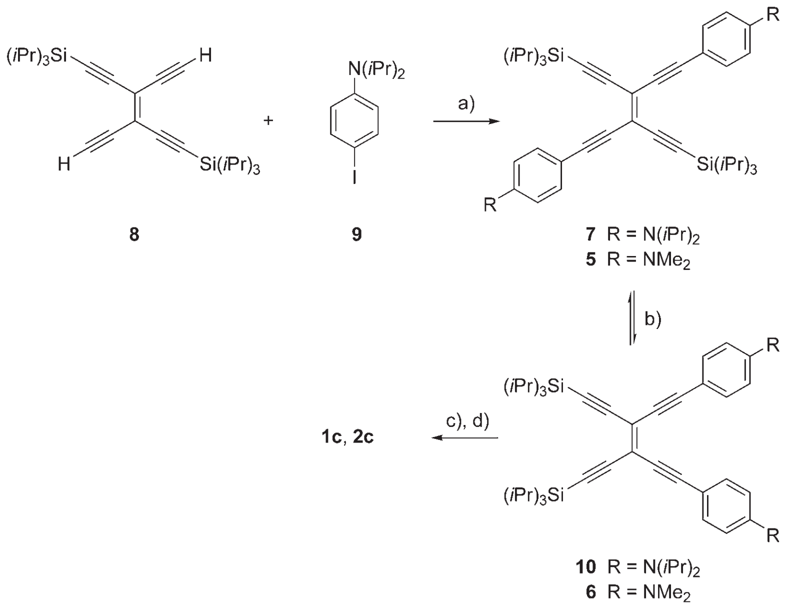
Results and Discusssion

Synthesis of 1c and 2c

The preparation of **1b**/**2b** involved the photochemical *E*→*Z* isomerization of **5**[16] to *cis*-TEE **6** (Scheme 1; ≈40% *Z* and 50% *E* isomer were isolated from the irradiated 0.44 mM solutions), which subsequently had its silyl groups removed and was subjected to macrocyclization by oxidative coupling.[13d] However, on the larger scale required for the synthesis of the targeted expanded [20]- and [30]annulene perimeters, the separation of **5** and **6** was tedious and low-yielding due to the limited stability of *Z* isomer **6** during column chromatography (SiO_2). Furthermore, purification of larger amounts of starting *E* isomer **5**, formed by Sonogashira cross-coupling,[13d,16,17] required repetitive column chromatography, which also led to substantial loss of material.

We therefore turned to bulkier, sterically better protecting anilino donor groups. *N,N*-dihexylanilino residues did not prove to be very useful as separation of the *E* and *Z* isomers formed by photoisomerization was not possible on a preparative scale due to their similar polarity.[13d] Gratifyingly, *N,N*-diisopropylanilino groups were found to enhance suffi-



Scheme 1. Synthesis of dehydroannulenes **1c** and **2c**. a) [$PdCl_2(PPh_3)_2$], CuI, $(iPr)_2NH$, 21 h, 69%. b) *hν*, Et_2O, 2 h, 20 °C, 49% (**10**), 48% (**7**). c) nBu_4NF, THF, 15 min, 0 °C. d) CuCl, TMEDA, air, acetone, 2 h, 20 °C, 26% (**1c**), 46% (**2c**) (yields over two steps).

ciently the stability of the TEE derivatives while at the same time not causing additional problems with separation.

(*E*)-Bis-(*N*,*N*-diisopropylaniline)-substituted **7** was prepared in 69% yield by cross-coupling of TEE **8**[16a] with 4-iodo-*N*,*N*-diisopropylaniline (**9**; Scheme 1). The latter was not available by one-pot dialkylation of 4-iodoaniline with 2-iodopropane, but required the isolation of the intermediate 4-iodo-*N*-isopropylaniline, which was subjected to the second alkylation (22% yield over the two steps). Irradiation of **7** in Et_2O[13d,18] with a medium-pressure Hg lamp (125 W) for 2 h at 20 °C provided a mixture of *E* and *Z* isomers, which was readily separated by column chromatography (SiO_2) to yield **10** (49%) along with starting material **7** (48%). No signs of decomposition were observed during the workup and purification of **10**. Upon slow evaporation of a solution of *E*-configured TEE **7** in hexane, single crystals suitable for X-ray crystallographic analysis were formed. The compound crystallized in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The torsion angles C(Ph)−C(Ph)−N−C(*i*Pr) in two independent molecules are −26.9 and −12.4°, and −0.1 and 35.4°, respectively. The angles at the nitrogen atoms sum to 358.9 and 351.6°, which indicates a very small degree of pyramidalization at these atoms. The $Si(iPr)_3$ groups of both independent molecules show static and dynamic disorder that could not be resolved (see Supporting Information).

Deprotection of **10** with nBu_4NF in moist THF was immediately followed, without any purification, by oxidative Hay coupling.[19] Mass-spectrometric analysis (MALDI-TOF) of the crude product mixture indicated the formation of octadehydro[12]annulene **1c** and dodecadehydro[18]annulene **2c**, together with smaller quantities of higher macrocyclic oligomers (i.e. tetra-, penta-, and hexamer; see Supporting Information). Whereas the two macrocycles **1c** (26%) and **2c** (46%) were separated by column chromatography, attempts to isolate the higher oligomers were not successful.

Dehydroannulenes **1c** and **2c** are deep-purple metallic solids that are readily soluble in common organic solvents. Antiaromatic, strained **1c** can be stored in solution in CH_2Cl_2 at −20 °C for months, but deteriorates readily as a solid at 20 °C. On the other hand, **2c** did not show any signs of decomposition when kept as a solid at 20 °C over a period of months. In comparison to the previously reported synthesis of **1b** (2% yield) and **2b** (22% yield), the yields of both **1c** (26%) and **2c** (46%) obtained under similar conditions were significantly improved.[13c,d] Better solubility facilitated their purification, and the new *N*,*N*-diisopropylanilino donor groups conveyed much higher stability, as demonstrated, in particular, by the substantially higher yield of **1c** with its delicate [12]annulene chromophore.

Single crystals of **2c** suitable for X-ray crystallographic analysis were obtained by very slow evaporation of a solution in CH_2Cl_2/hexane at 20 °C. The compound crystallizes in the triclinic space group $P\bar{1}$ with one macrocycle and one CH_2Cl_2 molecule in the asymmetric unit. The central core of **2c** (C1 to C18) is practically planar with a maximum deviation from the corresponding mean plane of about 0.12 Å (Figure 1a). The phenyl rings, on the other hand, are all twisted with respect to this plane, with torsion angles of 14.7 (C96 to C101), 15.5 (C36 to C41), 25.2 (C81 to C86), 42.1 (C66 to C71), 63.7 (C21 to C26), and 68.8° (C51 to C56). A preliminary analysis suggests that this twisting may be caused, at least partly, by weak intermolecular C−H···π interactions involving C−H residues of phenyl rings and acetylenic moieties of neighboring molecules.[20] Two such interactions, between the phenyl ring C51 to C56 (showing the largest rotation out of the macrocyclic plane) and a neighboring molecule in the crystal packing of **2c**, are shown in Figure 1b. As a result, H53 undergoes two short contacts to the carbon atoms of the triple bond C9′−C10′ in the macrocyclic core, and H52 makes two short contacts to the exocyclic triple bond C64′−C65′. The corresponding C···H distances range from 2.66 to 3.01 Å, and the C···H−C angles from 125 to 157° (note that the H positions used for the present analysis are based on stereochemical considerations with C−H distances of 1.085 Å). The torsion angles C(Ph)−C(Ph)−N−C(*i*Pr) vary between −32.7 (C23−C24−N27−C31) and +27.5° (C98−C99−N102−C103). Pyramidalization of the ni-

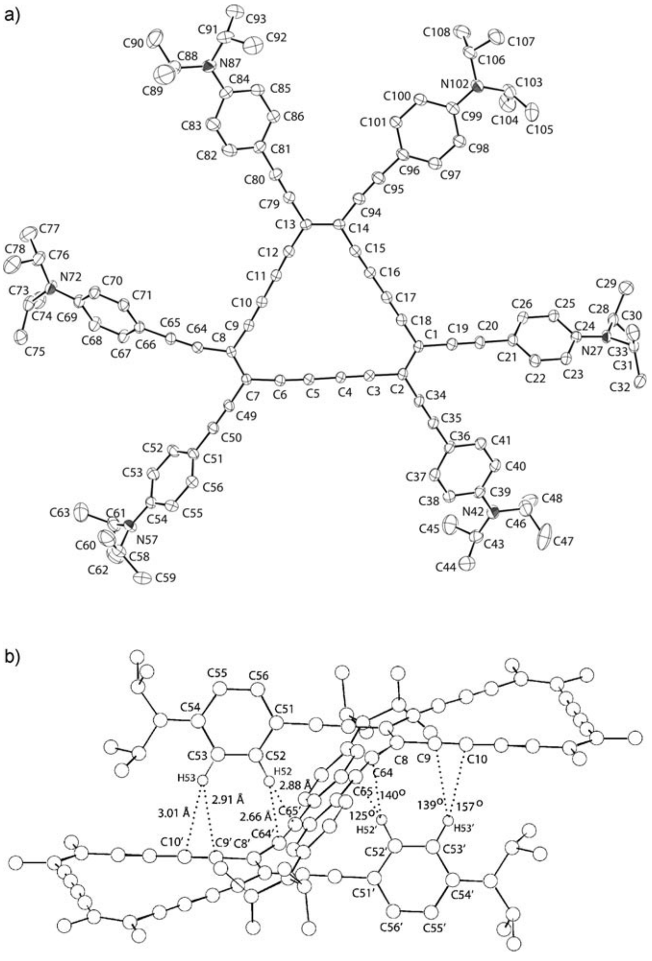


Figure 1. a) ORTEP plot of **2c**; arbitrary numbering, H atoms and solvent molecule are omitted for clarity. Atomic displacement parameters at 223 K are drawn at the 30 % probability level. Selected bond lengths (Å): C1–C2 1.387(5), C2–C3 1.416(5), C3–C4 1.214(5), C4–C5 1.350(5), C5–C6 1.221(5), C6–C7 1.410(5), C7–C8 1.390(4), C2–C34 1.414(5), C34–C35 1.214(5), C35–C36 1.420(5). Selected bond angles (°): C2–C1–C18 120.1(3), C1–C2–C3 120.3(3), C4–C3–C2 179.1(4), C3–C4–C5 179.9(4), C5–C6–C7 175.9(3), C65–C64–C8 168.6(3). The torsion angles C(Ph)–C(Ph)–N–C(*i*Pr) vary between −32.7 (C23–C24–N27–C31) and +27.5° (C98–C99–N102–C103). The sums of the three bond angles at the nitrogen atoms range between 357.9 (N102) and 359.8° (N42). b) Arrangement of neighboring molecules in the crystal packing of **2c** showing intermolecular C–H⋯π interactions.

trogen atoms is not significant. This is expressed by the sums of the three bond angles at these nitrogen atoms, which range from 357.9° (N102) to 359.8° (N42). Interestingly, one of the exocyclic C≡C–C(sp^2) moieties, namely C65–C64–C8, is considerably bent based on its bond angle of 168.6°, presumably due to the above mentioned C–H⋯π interactions and additional crystal-packing effects (Figure 1 b).

Synthesis of 3 and 4

Removal of the Si(*i*Pr)$_3$ groups in **10** with *n*Bu$_4$NF, followed by Cadiot–Chodkiewicz coupling[19b,21] with 1-bromo-2-(triisopropylsilyl)ethyne,[22] furnished the elongated TEE derivative **11** in good yield (57 %) as an air- and light-stable deep-red solid (Scheme 2). The Si(*i*Pr)$_3$ protecting groups were removed (*n*Bu$_4$NF), and the free bis(buta-1,3-diyne) was subjected to oxidative Hay coupling without further purification. The crude mixture obtained in the macrocyclization was examined by MS (MALDI), which indicated the formation of macrocycles **3** and **4** but not of any higher cyclic oligomers. Separation by column chromatography (SiO$_2$, hexanes/Et$_2$O = 1:1) afforded dehydro[20]annulene **3** (6 %) and dehydro[30]annulene **4**. The latter was further purified by size-exclusion chromatography (bio-beads SX-3, THF) to give pure **4** in 13 % yield. Both macrocycles are only sparingly soluble in hexanes/Et$_2$O (1:1); nevertheless, this is the only solvent mixture that gave reasonable chromatographic separation of **3** and **4**. The solubility problems during purification are a major reason for the low yields of the isolated pure dehydroannulenes.

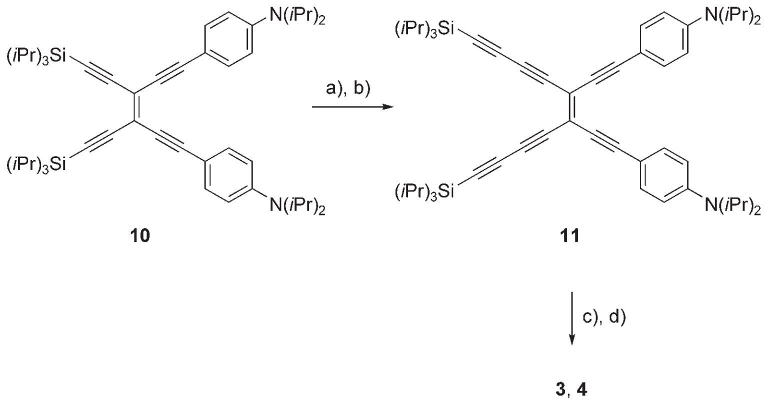
Both **3** and **4** were obtained as deep-purple metallic solids that are readily soluble in chlorinated organic solvents. The stability of the rather strained **3** is limited: it decomposed even in solution in CH$_2$Cl$_2$ kept at −20 °C; after several weeks, black insoluble material of unknown composition was obtained. In contrast, **4** showed higher stability and can be kept in the solid state at 20 °C for a couple of days without significant signs of decomposition.

The identity of **3** and **4** was confirmed by HRMS (MALDI-FT) and ^{1}H and ^{13}C NMR spectroscopy. During the characterization of **1c**, **2c**, **3**, and **4** by ^{1}H NMR spectroscopy in CDCl$_3$, no concentration dependence of the chemical shifts of the aromatic protons was observed. This indicates the absence of self-association within the concentration range studied (0.1–5.0 mM), in agreement with the electronic absorption behavior, which obeys the Beer–Lambert law (see below).

UV/Vis Spectroscopy

In previous work,[13c,d] we had observed that the replacement of terminal silyl groups in **1a** and **2a** by *N*,*N*-dialkylanilino donor groups resulted in dramatic spectral changes. New intense, longer-wavelength absorptions appeared in the UV/Vis spectra of **1b** and **2b** that were identified as CT bands resulting from intramolecular charge transfer from the peripheral electron-donating anilino groups to the electron-accepting all-carbon core. The UV/Vis spectra of the newly prepared donor-substituted dehydroannulenes **1c**, **2c**, **3**, and **4** in CH$_2$Cl$_2$ are displayed in Figure 2.

At first sight, the spectra of all the macrocycles are dominated by an intense, broad CT band at $\lambda_{max} = 552 \pm 2$ nm, with end absorptions at around 800 nm (1.55 eV). Interestingly, this band is more intense in the spectrum of **2c** (λ_{max} = 553 nm (2.24 eV), $\varepsilon = 136\,100\,\mathrm{M^{-1}\,cm^{-1}}$) than in the spectrum of the more-extended **4** (λ_{max} = 554 nm (2.24 eV), $\varepsilon = 89\,800\,\mathrm{M^{-1}\,cm^{-1}}$). The band is clearly weakest in the spectra of **3** (λ_{max} = 552 nm (2.24 eV), $\varepsilon = 41\,100\,\mathrm{M^{-1}\,cm^{-1}}$) and **1c** ($\lambda_{max}$ = 550 nm (2.25 eV), $\varepsilon = 34\,400\,\mathrm{M^{-1}\,cm^{-1}}$). In agreement with the concentration-independent NMR spectra (see



Scheme 2. Synthesis of dehydroannulenes **3** and **4**. a) nBu$_4$NF, THF, 20 min, 0°C. b) CuCl, nBuNH$_2$, NH$_2$OH·HCl, 1-bromo-2-(triisopropylsilyl)ethyne, *N*,*N*-dimethylformamide (DMF), 26 h, 20°C, 57%. c) nBu$_4$NF, THF, 15 min, 0°C. d) CuCl, TMEDA, air, acetone, 2 h, 20°C, 6% (**3**), 13% (**4**) (yields over two steps).

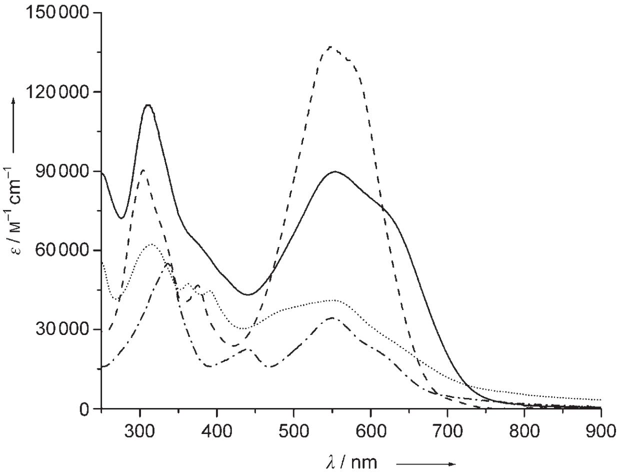


Figure 2. UV/Vis spectra of dehydroannulenes **1c**, **2c**, **3**, and **4** in CH$_2$Cl$_2$. -•-• **1c**, --- **2c**, ••••• **3**, —— **4**.

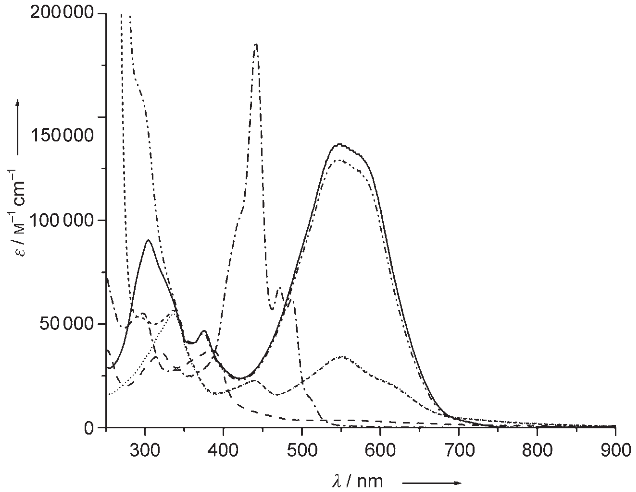


Figure 3. UV/Vis spectra of **1c** and **2c** in CH$_2$Cl$_2$ recorded neat, after acidification with *p*-toluenesulfonic acid, and after reneutralization with triethylamine. ••••• **1c**, --- **1c** acidified, ----- **1c** neutralized, —— **2c**, -•-• **2c** acidified, -••- **2c** neutralized.

above), no deviations from the Beer–Lambert law were observed within the concentration range studied (2×10^{-6}–2×10^{-5} M), thus indicating that the macrocycles are unable to undergo any kind of self-aggregation in CH$_2$Cl$_2$.

In comparison to the *N*,*N*-dimethylanilino-substituted analogues **1b** and **2b**,[13c,d] the longest-wavelength absorption maxima of **1c** and **2c** are bathochromically shifted by more than 30 nm, presumably due to the stronger electron-donating ability of the *N*,*N*-diisopropylanilino groups.[23]

The charge-transfer character of the longest-wavelength absorption bands in all four dehydroannulenes was confirmed in protonation experiments. When solutions of these compounds in CH$_2$Cl$_2$ were acidified with *p*-toluenesulfonic acid (Figures 3 and 4; see also Supporting Information), the color changed from purple to yellow. The intense bands at $\lambda_{max}=552\pm2$ nm nearly completely disappeared, and the new absorptions were substantially hypsochromically shifted. Neutralization with triethylamine regenerated nearly quantitatively the original spectra (Figures 3 and 4).

These protonation experiments not only confirm the CT character of the longest-wavelength bands but also provide a glimpse of the chromophoric properties of the perethynylated dehydroannulenes, which are unperturbed by donor–acceptor interactions. The two $4n+2$ π-electron systems clearly show a different spectral behavior to the two $4n$ ones. In the case of the $4n$ π chromophores **1c** and **3**, broadened bands are generated upon protonation, with the first strong maxima appearing at around 400 nm. In contrast, the spectra of the protonated $4n+2$ π-electron chromophores **2c** and **4** feature highly structured, very intense bands, with the longest-wavelength maximum of **4** ($\lambda_{max}=471$ nm (2.63 eV), $\varepsilon=96300\,\mathrm{M^{-1}cm^{-1}}$) appearing at a lower energy than in the spectrum of **2c** ($\lambda_{max}=441$ nm (2.81 eV), $\varepsilon=186000\,\mathrm{M^{-1}cm^{-1}}$). The spectra of protonated **1c** and **2c** expectedly resemble those previously recorded for protonated **1b** and **2b**, respectively.[13d]

The nature of the conjugated macrocyclic π-electron perimeter also seems to influence the efficiency of the intramolecular charge-transfer interaction, as expressed by the intensity of the CT band (Figure 2). If this efficiency is solely determined by the extension of the macrocyclic, electron-accepting perimeter and the number of donor–acceptor paths, the intensity of the CT band would increase in the sequence [12]annulene **1c** < [18]annulene **2c** < [20]annulene **3** < [30]annulene **4**. Experimentally, however, the intensities

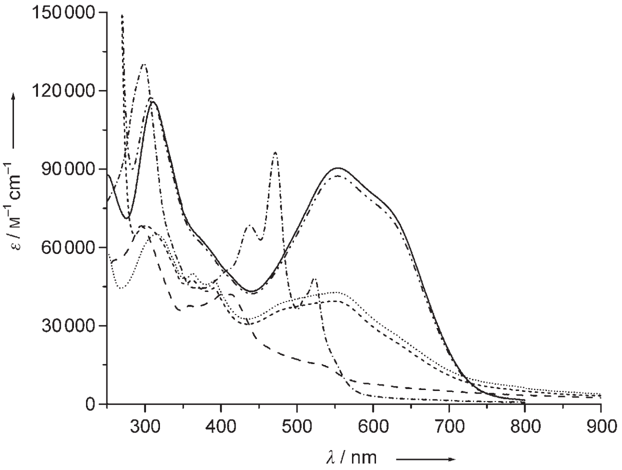


Figure 4. UV/Vis spectra of **3** and **4** in CH_2Cl_2 recorded neat, after acidification with *p*-toluenesulfonic acid, and after reneutralization with triethylamine. ••••• **3**, ––– **3** acidified, ----- **3** neutralized, —— **4**, –•–• **4** acidified, –··– **4** neutralized.

of the CT bands of the two $4n+2$ perimeters **2c** and **4** are much higher than those of the two $4n$ perimeters **1c** and **3**. At present, we do not have a good explanation for this unprecedented finding.

Table 1. Electrochemical data of *N*,*N*-diisopropylanilino-substituted TEE dehydroannulenes observed by CV and RDV in CH_2Cl_2 (with 0.1 M nBu$_4$NPF$_6$).[a]

	CV			RDV	
	$E°$ [V][b]	ΔE_p [mV][c]	E_{pc} [V][d]	$E_{1/2}$ [V][e]	Slope [mV][f]
1c	+0.40	100		+0.44 (2e$^-$)	100
	+0.24	60		+0.24 (2e$^-$)	60
	−1.14	70		−1.17 (1e$^-$)	80
	−1.48	80		−1.52 (1e$^-$)	75
2c			+0.37	+0.30 (3e$^-$)	85
	−1.31	70		−1.32 (1e$^-$)	60
	−1.63	80		−1.65 (1e$^-$)	60
			−2.43		
3			+0.64[g]	+0.67 [h]	
	+0.34	60		+0.35	80
			−0.98	−1.02	
			−1.18	−1.21	
4			+0.40		
			−1.20		
			−1.35		
			−1.63		
7	+0.32	100		+0.35 (2e$^-$)	75
	−1.98	80		−1.98	70
			−2.50		
10	+0.33	95		+0.38 (2e$^-$)	100
	−1.98	70		−2.00 (1e$^-$)	70
			−2.53		
11	+0.38	60		+0.37 (2e$^-$)	80
	+0.33	60			
	−1.62	75		−1.63 (1e$^-$)	60
			−2.27	−2.18	120

[a] All potentials are given versus the Fc$^+$/Fc couple as internal standard. [b] $E° = (E_{pc}+E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [c] $\Delta E_p = E_{ox} - E_{red}$, where the subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively. [d] E_{pc} = irreversible peak potential. [e] $E_{1/2}$ = half-wave potential. [f] Slope = slope of the linearized plot of E versus $\log[I/(I_{lim}-I)]$, where I_{lim} is the limiting current and I the current. [g] Small amplitude signal. [h] Not a well-defined wave due to electrode inhibition during oxidation.

Electrochemistry

The redox properties of **1c**, **2c**, **3**, and **4** as well as their precursors **7**, **10**, and **11** were studied by cyclic voltammetry (CV) and rotating-disc voltammetry (RDV). The measurements were carried out in CH_2Cl_2 with nBu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte. All potentials are given against Fc$^+$/Fc (ferricinium/ferrocene couple) as an internal reference and are uncorrected from ohmic drop (Table 1).

The *N*,*N*-diisopropylanilino-substituted TEEs **7**, **10**, and **11**, similar to the *N*,*N*-dimethylanilino derivatives **5**[24b] and **6** (see Supporting Information), gave well-resolved voltammograms. They undergo two reduction steps: a reversible one-electron transfer followed by an irreversible multielectron step close to the electrolyte discharge. Oxidation occurs in a single reversible two-electron transfer on the two *N*,*N*-diisopropylanilino groups. In the case of **5** and **6**, the oxidation peak current ratio I_{pc}/I_{pa} is beyond unity for low scan rates, and reaches unity for scan rates higher than 1 V s^{-1}. This behavior is characteristic for an electrochemical–chemical (EC) mechanism, with the generated oxidized species undergoing a chemical reaction (see Supporting Information). On the other hand, for the N(iPr)$_2$ derivatives, no followup chemical reaction could be observed on the time scale of CV. It seems that replacing the methyl groups with isopropyl chains stabilizes the electrogenerated dicationic species.

Optically transparent thin-layer electrode (OTTLE) studies of the first reduction steps for **7** and **10** gave nice spectral evolutions with well-defined isosbestic points (see Supporting Information). The reversibility of the process could be confirmed, as the initial spectrum was recovered quantitatively after reoxidation. Time-resolved OTTLE spectra during the oxidation of **7** and **10** clearly indicate that the generated dications are unstable and undergo a chemical reaction. However, the spectra observed for the dication of **7** and **10** are identical, with absorption bands at 456, 487, and 777 nm (see Supporting Information). Reduction of the electrogenerated species could not regenerate quantitatively the initial spectrum. Only 70% of the initial spectrum could be recovered for **7**. In contrast, the final spectrum of **10** after reduction shows only one main band at 482 nm that is typical for the *E* derivative **7** (see Supporting Information). It is clear that although the generated dication is not very stable, an electrochemically induced isomerization occurs during the oxidation of **10** to generate the more stable *E* isomer **7**. Such isomerization had been observed in the case of bis(4-nitrophenyl)-substituted TEEs.[24a]

The increased stability of *N*,*N*-diisopropylanilino-substituted dehydro[12]annulene **1c** allowed for the first time the exploration of the redox properties of a donor-substituted antiaromatic π system (for the CV traces, see Supporting Information). Thus, **1c** was reduced in two reversible one-electron steps (−1.14 and −1.48 V) and oxidized in two two-electron oxidation steps (+0.24 and +0.40 V). Aromatic dodecadehydro[18]annulene **2c** was reduced in two one-electron reversible steps at −1.31 and −1.63 V, the third reduction being an irreversible multielectron step. Only one oxidation could be observed. This oxidation is irreversible at scan rates below 0.1 $V s^{-1}$, and becomes reversible at scan rates higher than 5 $V s^{-1}$, thus indicating an EC oxidation mechanism. The comparison of the peak amplitude obtained by CV and the limiting currents observed by RDV for the first reduction and the first oxidation indicates that the oxidation involves only three electrons. No additional signal is observed for the remaining *N*,*N*-diisopropylanilino group. It is not excluded that electrode inhibition or low solubility of the generated trication in CH_2Cl_2 precludes the observation of the expected further oxidation.

Antiaromatic **3** underwent film formation during electrochemical investigations. Nevertheless, reproducible voltammograms could be obtained for the first scan on newly polished electrodes. The observed peak potentials under these conditions are listed in Table 1. Oxidation occurs in two steps, the first one being reversible for scan rates higher than 1 $V s^{-1}$. The second oxidation is irreversible and of a small amplitude. We also showed by RDV that the first oxidation gave a well-defined wave, whereas the second step was inhibited by the formation of an insulating film. Such behavior may explain the small amplitude of the signal observed by CV. The reductions of **3** are not well-resolved, but the observed potentials are consistent with the structure of the studied species.

Aromatic macrocycle **4** undergoes one irreversible oxidation as well as several small-amplitude reduction steps as observed by CV. The peak currents and potentials are scan-dependent due to film formation on the electrode surface. Reproducible voltammograms could only be observed for the first scan carried out on a newly polished electrode. The observed peak potentials under these conditions are listed in Table 1. The single oxidation signal observed may correspond to the oxidation of the six *N*,*N*-diisopropylanilino substituents. Indeed, comparison with the behavior of the corresponding precursor **11**, oxidized in a two-electron step, shows a similar oxidation potential. It seems that the substituents are not conjugated with the central all-carbon core and as such behave as independent redox centres.

As a general trend in the whole series of compounds currently studied, one can see that the first oxidation potential is quite similar and characteristic of the oxidation of an *N*,*N*-diisopropylanilino group as observed previously.[24a] These substituents behave as quite independent redox centers, being only slightly affected by the electron-acceptor character of the remaining conjugated core. This is a sign of weak conjugative coupling between donor and acceptor moieties.[25]

In contrast, comparison of the first reduction potentials shows that an extension of the electron-accepting acetylenic π system from **10** to **11**, from **1c** to **3**, and from **2c** to **4** provokes an anodic shift for the first reduction potential, which is expected. Also, increasing the number of electron-donating *N*,*N*-diisopropylanilino substituents (**1c** vs. **2c** and **3** vs. **4**), shifts the first reduction potential to more-negative values. The reduction potentials of *N*,*N*-diisopropylanilino-substituted **1c** and **2c** are shifted towards more negative values by 150 to 200 mV in comparison to their $Si(iPr)_3$-substituted analogues **1a** and **2a**,[26] thus indicating the electron-donating effects of the *N*,*N*-diisopropylanilino groups (Table 1).

A careful analysis of the observed influence of the electron-donating anilino groups on the first reduction potentials of **1c**, **2c**, **3**, and **4** provides a deeper insight into the antiaromatic/aromatic characteristics of the studied dehydroannulenes. Going from antiaromatic **1c** to aromatic **2c**, the number of electron-donating *N*,*N*-diisopropylanilino groups is increased from four to six (similarly so on going from **3** to **4**). On account of this fact, it is quite difficult to quantify the potential shift corresponding to one electron-donating substituent. However, an average value may be obtained. Indeed, previous studies showed that for dehydroannulene **2b** (−1.36 V in THF), which bears six peripheral *N*,*N*-dimethylanilino substituents,[13c] a 240-mV shift compared to the $Si(iPr)_3$-substituted analogue **2a** (−1.12 V in THF),[13b] was observed. That implies a cathodic shift of roughly 40 mV (if additive) when one $Si(iPr)_3$ group is replaced by one *N*,*N*-dialkylanilino substituent. Similar evolutions between **1c**, which bears four electron-donating anilino groups, and its silylated counterpart gave a cathodic shift of 150 mV that is in good agreement with a 40-mV shift per *N*,*N*-dialkylanilino group. Taking into account the estimated value of 40 mV, increasing the number of donor substituents by two, when going from **1c** to **2c**, should shift the potential to more negative values by about 80 mV. However, the experimentally found (CV) difference between the first reduction potentials of **1c** and **2c** is 170 mV, which is much larger than the expected value. Even though the data for **3** and **4** are rather scarce, the effect of *N*,*N*-dialkylanilino substituents is expected to be the same. The difference between the first reduction potentials of **3** and **4** is 220 mV (although the CV traces showed that the reductions were irreversible). Based on the above-mentioned considerations, this difference should again be only about 80 mV (effect of two additional anilino groups). Therefore, it seems that the antiaromaticity of **1c** and **3** and the aromaticity of **2c** and **4** provide an explanation for the observed reduction behavior: it is easier to inject an electron into the antiaromatic $4n$ π-electron perimeters than into the aromatic $4n+2$ systems.[26]

Conclusions

By employing a photochemical route to *Z*-bisprotected donor-substituted TEEs,[13d] bis(*N*,*N*-diisopropylanilino)-substituted TEE **10**, with improved stability and solubility, was prepared for the construction of large dehydroannulenes. Yields in the macrocyclization of **10** to the perethynylated octadehydro[12]annulene **1c** and dodecadehydro[18]annulene **2c** are significantly improved compared to the yields previously obtained in the synthesis of the *N*,*N*-dimethylanilino-substituted dehydroannulenes **1b** and **2b**. This is readily explained by the enhanced solubility and stability provided by the diisopropylamino compared to the dimethylamino groups. The first X-ray crystal structure of an anilino-substituted dehydro[18]annulene was obtained, revealing a practically planar macrocyclic framework of **2c**. Pairs of macrocycles in the crystal lattice undergo multiple intermolecular C−H···π interactions involving the C−H residues of phenyl rings and acetylenic π bonds. Oxidative Hay coupling of elongated building block **11** after alkyne deprotection afforded the unprecedented expanded hexadecadehydro[20]annulene **3** and tetracosadehydro[30]annulene **4**, decorated and stabilized by peripheral electron-donating *N*,*N*-diisopropylanilino groups. UV/Vis spectroscopy furnished evidence for strong intramolecular charge-transfer interactions between the peripheral electron-donating anilino groups and the central electron-deficient cores. These interactions seem to be more effective in the $4n+2$ than the $4n$ π-electron chromophores. Electrochemical studies of the newly prepared dehydroannulenes demonstrated the electron-accepting power of their all-carbon cores. Careful analysis provided indications that the antiaromatic systems are more readily reduced than the aromatic counterparts, in agreement with previous findings.[26] The presented work clearly demonstrates once more the power and versatility of TEE building blocks for the modular construction of large, two-dimensional all-carbon sheets.

Experimental Section

Materials and General Methods

Reagents and solvents were purchased at reagent grade from Acros, Aldrich, and Fluka, and used as received. THF was freshly distilled from Na/benzophenone, and CH_2Cl_2 from CaH_2 under N_2. Hay catalyst refers to a freshly prepared solution of CuCl (100 mg, 1.0 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA; 0.15 mL, 1.0 mmol) in acetone (25 mL). All reactions except Hay couplings were performed under an inert atmosphere by applying a positive pressure of N_2 or Ar. Compound **8**[16a] and 1-bromo-2-(triisopropylsilyl)ethyne[22] were prepared according to the procedures in the literature. Column chromatography (CC) and plug filtrations were carried out with SiO_2 60 (particle size 0.040–0.063 mm, 230–400 mesh; Fluka) and distilled technical solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with SiO_2 60 F_{254} obtained from Macherey-Nagel; a UV lamp (254 or 366 nm) was used for visualization. Size-exclusion chromatography (GPC) was performed on bio-beads SX-3 from Bio-Rad. Melting points were measured on a Büchi B-540 melting-point apparatus in open capillaries and are uncorrected. "Decomp." refers to decomposition. Some melting/decomposition points could not be determined due to the low stability of the compounds. UV/Vis spectra were recorded on a Varian Cary-5 spectrophotometer. The spectra were recorded in CH_2Cl_2 or $CHCl_3$ in a quartz cuvette (1 cm). The absorption wavelengths are reported in nm with the extinction coefficient $\text{M}^{-1}\,\text{cm}^{-1}$ in brackets; shoulders are indicated as sh. Infrared spectra were recorded on a Perkin Elmer FT1600 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 300 or on a Bruker DRX500 spectrometer at 20 °C. Chemical shifts are reported in ppm relative to the signal of $SiMe_4$. Residual solvent signals in the ^{1}H and ^{13}C NMR spectra were used as an internal reference. Coupling constants (*J*) are given in Hz. The apparent resonance multiplicity is described as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), sept (septuplet), and m (multiplet). High-resolution (HR) EI-MS and ESI-MS spectra were recorded on a Hitachi-Perkin Elmer VG-Tribrid spectrometer and a Finnigan Mat TSQ 7000 spectrometer, respectively. HR FT-MALDI spectra were recorded on an IonSpec Ultima FT instrument with [(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) or 3-hydroxypicolinic acid (3-HPA) as matrix. The most important signals are reported in *m*/*z* units with *M* as the molecular ion. MALDI-TOF spectra were recorded on a Bruker Reflex 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

Electrochemical measurements were carried out at 20 °C in CH_2Cl_2 containing 0.1 M $n\text{Bu}_4\text{NPF}_6$ in a classical three-electrode cell. CH_2Cl_2 was purchased at spectroscopic grade from Merck, dried over molecular sieves (4 Å), and stored under Ar prior to use. $n\text{Bu}_4\text{NPF}_6$ was purchased at electrochemical grade from Fluka and used as received. The working electrode was a glassy carbon disk electrode (2 mm in diameter) used either motionless for CV (0.1–10 $\text{V}\,\text{s}^{-1}$) or as a rotating-disc electrode for RDV. The auxiliary electrode was a platinum wire, and the reference electrode was an aqueous Ag/AgCl electrode. All potentials are referenced to the Fc^+/Fc couple, used as an internal standard, and are uncorrected from ohmic drop. The accessible range of potentials on the glassy carbon electrode was +1.4 to −2.4 V versus Fc^+/Fc in CH_2Cl_2. The cell was connected to the computerized multipurpose electrochemical device AUTOLAB (Eco Chemie BV, Utrecht, The Netherlands) controlled by GPSE software running on a personal computer.

X-ray Crystallographic Analysis

The structures were solved by direct methods (SIRS-97)[27] and refined by full-matrix least-squares analysis (SHELXL-97)[28] using an isotropic extinction correction. All heavy atoms were refined anisotropically. H atoms were refined isotropically; H positions were based on stereochemical considerations.

7: Crystal data at 220(2) K for $C_{52}H_{78}N_2Si_2$, $M_r=787.34$: triclinic, space group $P\bar{1}$ (no. 2), $\rho_{\text{calcd}}=0.992\ \text{g}\,\text{cm}^{-3}$, $Z=2$, $a=12.0694(5)$, $b=12.6299(7)$, $c=17.9160(8)$ Å, $\alpha=92.044(4)$, $\beta=92.778(3)$, $\gamma=104.564(2)°$, $V=2636.9(2)$ Å^3. Bruker-Nonius Kappa-CCD diffractometer, MoK_α radiation, $\lambda=0.7107$ Å, $\mu=0.099\ \text{mm}^{-1}$. An orange crystal of **7** ($\approx 0.30\times0.25\times0.10\ \text{mm}^3$) was obtained by slow evaporation of a solution of **7** in hexane. Numbers of measured and unique reflections are 13250 and 8046, respectively ($R_{\text{int}}=0.050$). The Si(*i*Pr)$_3$ groups of both independent molecules exhibit static and dynamic disorder that could not be resolved. Final $R(F)=0.107$, $wR(F^2)=0.279$ for 515 parameters, 5336 reflections with $I>2\sigma(I)$, $6.97<\theta<24.16°$ (corresponding R values based on all 8046 reflections are 0.151 and 0.330, respectively).

2c: Crystal data at 223(2) K for $C_{102}H_{108}N_6{\cdot}CH_2Cl_2$, $M_r=1502.87$: triclinic, space group $P\bar{1}$ (no. 2), $\rho_{\text{calcd}}=1.050\ \text{g}\,\text{cm}^{-3}$, $Z=2$, $a=17.1470(4)$, $b=18.5800(5)$, $c=8.7780(5)$ Å, $\alpha=109.728(2)$, $\beta=101.812(2)$, $\gamma=113.563(2)°$, $V=4752.6(3)$ Å^3. Bruker-Nonius Kappa-CCD diffractometer, MoK_α radiation, $\lambda=0.7107$ Å, $\mu=0.115\ \text{mm}^{-1}$. A black crystal of **2c** ($\approx 0.25\times0.22\times0.10\ \text{mm}^3$) was obtained by very slow evaporation of a solution of **2c** in CH_2Cl_2/hexane. Numbers of measured and unique reflections are 18810 and 11496, respectively ($R_{\text{int}}=0.059$). Final $R(F)=0.073$, $wR(F^2)=0.181$ for 1123 parameters, 7810 reflections with $I>2\sigma(I)$, $7.48<\theta<22.49°$ (corresponding *R* values based on all 11496 reflections are 0.114 and 0.217, respectively).

CCDC-605747 (**7**) and CCDC-605748 (**2c**) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) or athttp://www.ccdc.cam.ac.uk/data request/cif.

Syntheses

4-Iodo-*N*-isopropylaniline: A mixture of 4-iodoaniline (2.00 g, 9.1 mmol), 2-iodopropane (24.9 g, 14.7 mL, 147 mmol), and Na_2CO_3 (2.24 g, 21.2 mmol) in ethanol (50 mL) was stirred for 30 h at 80 °C. The solvent was removed in vacuo, and the residue was mixed with hexane (200 mL) and filtered. The filtrate was concentrated in vacuo and subjected to CC (SiO_2, hexanes/EtOAc = 10:1) to afford the product (1.68 g, 71 %) as a colorless oil. $R_f = 0.46$ (SiO_2, hexanes/EtOAc = 10:1); UV/Vis ($CHCl_3$): λ_{max} (ε) = 262 (25300), 305 nm (2800 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 3401, 2962, 1586, 1491, 1315, 1293, 1292, 1249, 1181, 808 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.19 (d, *J* = 6.2 Hz, 6H), 3.48 (br s, 1H), 3.57 (m, 1H), 6.36 (dd, *J* = 6.8, 2.1 Hz, 2H), 7.40 ppm (dd, *J* = 6.8, 2.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.01, 44.33, 77.36, 115.58, 137.98, 147.23 ppm; MS (EI) (70 eV): *m/z* (%): 261.0 (70) $[M]^+$, 246.0 (100) $[M-CH_3]^+$; elemental analysis: calcd (%) for $C_9H_{12}IN$ (261.11): C 41.40, H 4.63, N 5.36; found: C 41.37, H 4.70, N 5.40.

9: 4-Iodo-*N*-isopropylaniline (1.68 g, 6.42 mmol), 2-iodopropane (10.9 g, 6.4 mL, 64.1 mmol), and Na_2CO_3 (1.23 g, 11.6 mmol) in ethanol (30 mL) were stirred for 46 h at 80 °C. The solvent was removed in vacuo, and the oily residue was purified by CC (SiO_2, hexanes/EtOAc = 15:1) to afford **9** (603 mg, 31 %) as a white solid. $R_f = 0.59$ (SiO_2, hexanes/EtOAc = 10:1); m.p.: 40.5–41.1 °C; UV/Vis ($CHCl_3$): λ_{max} (ε) = 278 (17900), 310 nm (sh, 2900 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 2968, 1584, 1495, 1384, 1367, 1317, 1293, 1189, 1153, 1123, 1024, 811, 786 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.8 Hz, 12H), 3.76 (sept, *J* = 6.8 Hz, 2H), 6.63 (dd, *J* = 7.0, 2.2 Hz, 2H), 7.42 ppm (dd, *J* = 7.0, 2.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.25, 47.49, 78.56, 120.01, 136.98, 147.53 ppm; ESI-MS: *m/z* (%): 304.2 (100) $[M+H]^+$; elemental analysis: calcd (%) for $C_{12}H_{18}IN$ (303.19): C 47.54, H 5.98, N 4.62; found: C 47.53, H 5.89, N 4.80.

7: **8** (500 mg, 1.14 mmol), $[PdCl_2(PPh_3)_2]$ (72 mg, 0.10 mmol), and CuI (33 mg, 0.17 mmol) were added to a degassed solution of **9** (694 mg, 2.29 mmol) in diisopropylamine (30 mL), and the mixture was stirred for 21 h at 20 °C. CH_2Cl_2 (200 mL) was then added, and the deep-red mixture filtered through a plug (SiO_2, CH_2Cl_2). The solvents were removed in vacuo, and the residue was purified by CC (SiO_2, toluene/hexanes = 20:1) to give **7** (615 mg, 69 %) as orange crystals. $R_f = 0.38$ (SiO_2, hexanes/EtOAc = 20:1); m.p.: 209.5–211.3 °C (decomp.); UV/Vis ($CHCl_3$): λ_{max} (ε) = 300 (36000), 344 (sh, 12400), 472 nm (46000 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 2939, 2863, 2197, 2141, 1599, 1515, 1418, 1369, 1329, 1293, 1138, 1116, 1016, 994, 882, 817 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.14 (s, 42H), 1.28 (d, *J* = 6.9 Hz, 24H), 3.86 (sept, *J* = 6.9 Hz, 4H), 6.74 (d, *J* = 9.0 Hz, 4H), 7.28 ppm (d, *J* = 9.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.48, 18.84, 21.22, 47.45, 87.02, 99.93, 100.09, 104.46, 109.82, 115.53, 115.75, 132.39, 148.32 ppm; HRMS (FT-MALDI) (DCTB): *m/z*: calcd for $C_{52}H_{78}N_2Si_2^+$: 786.5704 $[M]^+$; found: 786.5688; elemental analysis: calcd (%) for $C_{52}H_{78}N_2Si_2$ (787.37): C 79.32, H 9.98, N 3.56; found: C 79.33, H 9.93, N 3.61.

10: A solution of **8** (275 mg, 0.349 mmol) in Et_2O (140 mL) was irradiated with a medium-pressure Hg lamp (125 W) for 2 h at 20 °C. The dark-orange residue obtained by evaporation of the solvent in vacuo was subjected to CC (SiO_2, hexanes/EtOAc = 20:1) to yield **10** as an orange solid (134 mg, 49 %) and recovered **7** (133 mg, 48 %). $R_f = 0.29$ (SiO_2, hexanes/EtOAc = 20:1); m.p.: 70.4–72.5 °C; UV/Vis ($CHCl_3$): λ_{max} (ε) = 283 (sh, 26500), 305 (30200), 412 (30500), 470 nm (30300 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 2941, 2864, 2178, 2132, 1602, 1516, 1463, 1418, 1368, 1329, 1292, 1188, 1115, 1016, 996, 883, 818 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.13 (s, 42H), 1.28 (d, *J* = 6.9 Hz, 24H), 3.88 (sept, *J* = 6.9 Hz, 4H), 6.76 (d, *J* = 9.0 Hz, 4H), 7.32 ppm (d, *J* = 9.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.51, 18.88, 21.26, 47.50, 87.44, 100.15, 100.38, 104.41, 109.89, 115.42, 115.62, 132.43, 148.40 ppm; HRMS (MALDI) (DCTB): *m/z* calcd for $C_{52}H_{78}N_2Si_2^+$: 786.5704 $[M]^+$; found 786.5708; elemental analysis: calcd (%) for $C_{52}H_{78}N_2Si_2$ (787.37): C 79.32, H 9.98, N 3.56; found: C 79.42, H 9.94, N 3.39.

1c and **2c**: nBu_4NF (1 M in THF, 0.35 mL) was added to a cooled solution (0 °C) of **10** (90 mg, 0.114 mmol) in moist THF (10 mL). After the mixture was stirred for 15 min, CH_2Cl_2 (50 mL) was added, and the mixture was filtered through a plug (SiO_2, CH_2Cl_2). The solvents were evaporated in vacuo, and the residue was dissolved in acetone (150 mL). Hay catalyst (3 mL) was added, and the mixture was stirred while exposed to air for 2 h at 20 °C. The deep-purple solution was filtered through a plug (SiO_2, acetone) and evaporated in vacuo. The residue was subjected to CC (SiO_2, CH_2Cl_2/EtOAc = 1→2 %) to afford **1c** (14.1 mg, 26 %) and **2c** (24.8 mg, 46 %), both as deep-purple metallic solids. **1c**: $R_f = 0.79$ (SiO_2, CH_2Cl_2/EtOAc = 1 %); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 336 (55100), 440 (22700), 550 (34400), 600 nm (23000 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 2926, 2863, 2152, 2128, 1595, 1515, 1406, 1368, 1329, 1292, 1186, 1152, 1112, 1019, 965, 936, 816 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (d, *J* = 6.8 Hz, 48H), 3.87 (sept, *J* = 6.8 Hz, 8H), 6.70 (d, *J* = 9.0 Hz, 8H), 7.22 ppm (d, *J* = 9.0 Hz, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.07, 47.45, 84.90, 87.94, 94.72, 104.71, 108.82, 115.74, 121.50, 132.68, 148.94 ppm; HRMS (MALDI) (DCTB): *m/z* calcd for $C_{68}H_{72}N_4^+$: 944.5757 $[M]^+$; found: 944.5764. **2c**: $R_f = 0.68$ (SiO_2, CH_2Cl_2/EtOAc = 2 %); m.p.: 218 °C (decomp.); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 304 (90400), 375 (46700), 553 (136100), 573 nm (sh, 131000 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 2968, 2931, 2160, 1596, 1515, 1407, 1367, 1328, 1292, 1185, 1151, 1136, 1115, 1066, 1017, 815 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (d, *J* = 6.9 Hz, 72H), 3.93 (m, 12H), 6.81 (d, *J* = 9.0 Hz, 12H), 7.47 ppm (d, *J* = 9.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.31, 47.65, 83.75, 85.83, 87.16, 105.20, 109.35, 115.59, 116.38, 133.07, 149.16 ppm; HRMS (MALDI) (DCTB): *m/z* calcd for $C_{102}H_{108}N_6^+$: 1417.8669 $[M]^+$; found: 1417.8653; elemental analysis: calcd (%) for $C_{102}H_{108}N_6$ (1418.02): C 86.40, H 7.68, N 5.93; found C 86.39, H 7.75, N 5.97.

11: nBu_4NF (1 M in THF, 1.90 mL) was added to a cooled solution (0 °C) of **10** (500 mg, 0.635 mmol) in moist THF (30 mL). After the mixture was stirred for 20 min, CH_2Cl_2 (100 mL) was added, the mixture was filtered through a plug (SiO_2, CH_2Cl_2), and the solvents were removed in vacuo. The residue was dissolved in dry DMF (130 mL), and $NH_2OH{\cdot}HCl$ (441 mg, 6.35 mmol), butylamine (1.39 g, 1.90 mL, 19.1 mmol), and 1-bromo-2-(triisopropylsilyl)ethyne (1.66 g, 6.35 mmol) were added. The mixture was thoroughly degassed (three freeze–pump–thaw cycles). CuCl (629 mg, 6.35 mmol) was added, and the mixture stirred for 26 h at 20 °C. The mixture was poured into H_2O (1 L), saturated aqueous NaCl (200 mL) was added, and the mixture extracted with EtOAc (5 × 200 mL). The combined organic layers were washed with saturated aqueous NaCl (2 × 250 mL), dried ($MgSO_4$), and concentrated in vacuo to leave a deep-red solid. CC (SiO_2, hexanes/EtOAc = 10:1) afforded **11** (305 mg, 57 %) as a deep-red solid. $R_f = 0.25$ (SiO_2, hexanes/EtOAc = 20:1); m.p.: 78.2–81.0 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 307 (39000), 326 (sh, 32300), 364 (sh, 14500), 388 (14500), 462 (21300), 536 nm (27300 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 2940, 2864, 2161, 2088, 1600, 1516, 1463, 1418, 1368, 1329, 1293, 1187, 1153, 1117, 1016, 996, 882, 818 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.10 (s, 42H), 1.28 (d, *J* = 6.9 Hz, 24H), 3.89 (sept, *J* = 6.9 Hz, 4H), 6.74 (d, *J* = 9.0 Hz, 4H), 7.34 ppm (d, *J* = 9.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.49, 18.75, 21.27, 47.60, 73.31, 82.69, 86.64, 89.88, 93.12, 104.01, 109.10, 115.52, 116.97, 132.92, 149.09 ppm; HRMS (ESI): *m/z* calcd for $C_{56}H_{79}N_2Si_2^+$: 835.5782 $[M+H]^+$; found: 835.5765; elemental analysis: calcd (%) for $C_{56}H_{78}N_2Si_2$ (835.42): C 80.51, H 9.41, N 3.35; found: C 80.26, H 9.29, N 3.28.

3 and **4**: nBu_4NF (1 M in THF, 0.90 mL) was added to a cooled solution (0 °C) of **11** (250 mg, 0.300 mmol) in moist THF (25 mL). After the mixture was stirred for 15 min, TLC (SiO_2, hexanes/EtOAc = 10:1) indicated complete deprotection. CH_2Cl_2 (100 mL) was added, and the mixture was filtered through a plug (SiO_2, CH_2Cl_2). The solvents were removed in vacuo, and the oily residue was dissolved in acetone (850 mL). Hay catalyst (58 mL) was added, and the mixture was stirred while exposed to air for 2 h at 20 °C. The deep-purple solution was diluted with CH_2Cl_2 and filtered through a plug (SiO_2, CH_2Cl_2). The solvents were evaporated in vacuo to leave a deep-purple solid, which was subjected to CC (SiO_2, hexanes/Et_2O = 1:1) to yield **3** (8 mg, 6 %) and impure **4,** which was subsequently further purified by preparative GPC (bio-beads SX-3, THF) to give pure **4** (16 mg, 13 %). Both **3** and **4** are deep-purple metallic solids. **3**: $R_f = 0.46$ (SiO_2, hexanes/Et_2O = 1:1); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 316 (62200), 363 (47400), 391 (44700), 481 (sh, 36900), 552 nm (41100 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 2956, 2924, 2864, 2161, 2079, 1598, 1515, 1460, 1367, 1329, 1292, 1176, 1149, 1114, 1018, 817 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.28 (d, *J* = 6.9 Hz, 48H), 3.88 (sept, *J* = 6.9 Hz, 8H), 6.71 (d, *J* = 9.1 Hz, 8H), 7.24 ppm (d, *J* = 9.1 Hz, 8H); ^{13}C NMR

(125 MHz, $CDCl_3$): $\delta = 21.06$, 47.49, 69.60, 73.90, 83.50, 84.90, 84.95, 106.43, 108.38, 115.22, 120.94, 132.83, 149.17 ppm; HRMS (MALDI) (DCTB): m/z calcd for $C_{76}H_{72}N_4^+$: 1040.5752 $[M]^+$; found: 1040.5769. **4**: $R_f = 0.25$ (SiO_2, hexanes/$Et_2O = 1{:}1$); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 311 (115500), 374 (sh, 63000), 554 (89800), 614 nm (sh, 76400 $\text{M}^{-1}\,\text{cm}^{-1}$); IR (neat): $\tilde{\nu} = 2962$, 2925, 2863, 2147, 2074, 1594, 1514, 1413, 1367, 1327, 1290, 1183, 1136, 1112, 816 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.31$ (d, $J = 6.9$ Hz, 72H), 3.91 (sept, $J = 6.9$ Hz, 12H), 6.77 (d, $J = 9.0$ Hz, 12H), 7.38 ppm (d, $J = 9.0$ Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 21.10, 47.51, 66.46, 72.57, 76.15, 82.76, 86.70, 106.57, 108.67, 115.31, 117.21, 132.94, 149.20 ppm; HRMS (MALDI) (DCTB): m/z calcd for $C_{114}H_{108}N_6^+$: 1560.8630 $[M]^+$; found: 1560.8599.

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