186. Donor/Acceptor-Substituted Tetraethynylethenes: Systematic Assembly of Molecules for Use as Advanced Materials

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A comprehensive series of tetraethynylethenes (= 3,4-diethynylhex-3-ene-1,5-diynes, TEEs) bearing electron-donating (*p*-methoxyphenyl or *p*-aminophenyl) and/or electron-accepting (*p*-nitrophenyl) groups was prepared *via* [Pd]-catalyzed *Sonogashira* cross-coupling reactions. The electronic and photonic properties of these molecules were investigated with a special emphasis on the effects caused by degree and pattern of donor/acceptor substitution around the central TEE core. This analysis showed that intramolecular donor-acceptor interactions, as evidenced by a long-wavelength charge-transfer band, are considerably more effective in TEEs **44** and **46**, with *trans* and *cis*, linearly-conjugated electronic pathways between donor and acceptor, than in **11**, with a geminal, cross-conjugated electronic pathway. UV/VIS Spectroscopy revealed a steady bathochromic shift of the longest-wavelength absorption band (λ_{max}) as the number of donor-acceptor conjugation paths increased upon changing from bis-arylated (**11**, **44**, and **46**) to tetrakis-arylated (**14**, **31**, and **35**) TEEs. The position of the longest-wavelength absorption was also found to be strongly dependent on the nature of the N-substituents in the $R_2NC_6H_4$-donor groups. Electronic emission spectroscopic investigations demonstrated a considerable solvent dependency of the fluorescence of donor-acceptor-substituted TEEs such as **11** or **44**, in agreement with the presence of highly polarized excited states in these molecules. Correspondingly, fluorescence spectra of TEEs bearing only donor or acceptor substituents showed little solvent dependency. The large majority of the donor/acceptor-substituted TEEs are thermally and environmentally stable molecules. They can be stored for months as solids in the air at room temperature, and many decompose only upon heating to temperatures above 200°. X-Ray analysis showed the conjugated C-atom scaffolds of **44**, **46**, and **67** to be essentially planar, whereas the aryl substituents in **28** and **30** are rotated out of the plane of the TEE core by varying degrees.

1. Introduction. – Conjugated organic molecules and polymers show great promise as components for advanced electronic and photonic applications [1–3]. For the rational design of tailor-made organic materials with specific function, it is necessary to develop a profound understanding of how and to what degree changes in molecular electronic structure affect physical properties [4].

Tetraethynylethene (= 3,4-diethynylhex-3-ene-1,5-diyne, TEE **1**) provides a unique C-atom framework for the incorporation of functional groups into planar, fully conjugated, two-dimensional π-chromophores [5–8]. Essentially every desired substitution pattern on the TEE core can be achieved through the proficient use of various (trialkylsilyl)alkyne-protecting groups. Together, these molecules make up a 'molecular construction kit' which has been readily elaborated into acyclic [9] and cyclic [10] acetylenic molecular scaffolding, formation of oligomers [9] and polymers [11] with the conjugated poly(triacetylene) backbone, and preparation of highly ordered charge-transfer complexes in the solid state as well as in solution [12].

To enhance the appeal of TEEs as materials for electronics and photonics, the synthesis of donor- and/or acceptor-substituted derivatives (donor groups = p-$R_2NC_6H_4$, p-$MeOC_6H_4$, C_6H_5; acceptor groups = p-$O_2NC_6H_4$) was pursued and a comprehensive library of arylated TEE chromophores was reported in [13] [14]. The pattern and number of the substituted aryl rings on the TEE core was varied to include compounds displaying all possible donor-acceptor conjugation paths (*Fig. 1*). *trans*- or *cis*-Bis-functionalization provided one-dimensional linear conjugation (paths *a* and *b*), two geminally-oriented substituents afforded one-dimensional, cross-conjugation (path *c*), and substitution at all four terminal alkynes gave rise to full, two-dimensional conjugation [15] [16a] through the combination of four linear (*a* and *b*) and two cross-conjugated pathways (*c*). The orientation of donor/acceptor substituents about the TEE core and the degree of functionalization were shown to play a decisive role in determining the electronic and second- and third-order nonlinear optical properties of these molecules [16].

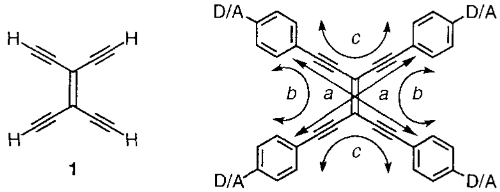


Fig. 1. *Tetraethynylethene* (**1**) *and schematic representation of possible conjugation pathways in perarylated tetraethynylethenes.* Paths *a* and *b* depict *trans*- and *cis*-linear conjugation, respectively, and path *c* depicts geminal cross-conjugation. D = donor. A = acceptor.

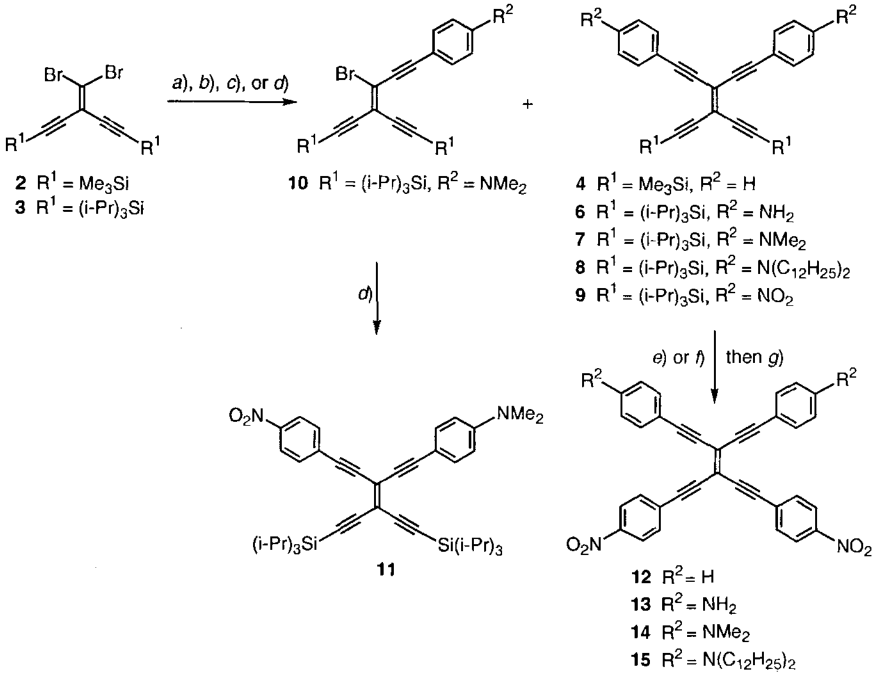
In this paper, we provide a full account of the synthesis and characterization of this library of donor/acceptor-functionalized TEEs. A fundamental examination of structure-function relationships for these molecules is described. Included in these analyses are the evaluation of thermal stabilities as measured by melting and decomposition temperatures and differential scanning calorimetry (DSC), structure determinations by X-ray crystallography and ^{13}C-NMR spectroscopy, and the elucidation of electronic and optical molecular properties by UV/VIS and fluorescence spectroscopy.

2. Results and Discussion. – 2.1. *General Considerations for the Synthesis of Aryl-Substituted Tetraethynylethenes.* As a general synthetic strategy, we sought to first prepare the TEE C-atom core by employing protocols previously developed in our laboratory [6] and then attach the p-donor- and/or p-acceptor-substituted Ph rings by Pd-catalyzed acetylenic cross-coupling reactions. Numerous methods are available for the cross-coupling of aryl or vinyl halides with terminal alkynes, and these procedures employ a plethora of Pd catalysts [17–20]. For the current syntheses, however, the *Sonogashira* cross-coupling using $[PdCl_2(PPh_3)_2]$/CuI as catalyst in Et_3N was viewed as the one which would combine high yields with experimental simplicity [21].

As had been previously reported for [Pd]-catalyzed alkynylations [22] [23], it was determined that electron-deficient aryl iodides such as p-iodonitrobenzene couple more rapidly and efficiently than electron-rich ones such as p-iodo-*N*,*N*-dialkylanilines. It was also determined that purification of mono- and bis-arylated TEEs is substantially more facile than that of tris- and tetrakis-arylated derivatives, mainly due to the low solubility of the latter. Therefore, in the synthesis of tris- and tetrakis-arylated compounds, we first performed the more difficult couplings to the *p*-NH_2 amino- or *p*-MeO-substituted aryl iodides, followed by the cleaner couplings to *p*-iodonitrobenzene in the last steps.

2.2. *Synthesis of Arylated Tetraethynylethenes.* The symmetrical, geminally bis-aryl-substituted TEEs **4** and **6**–**9** were synthesized by cross-coupling the known dibromo-olefins **2** [6a] or **3** [24] to the corresponding aryl acetylenes (*Scheme 1*). The synthesis of the parent diphenyl derivative **4** from **2** was previously reported [6a]; however, application of the *Sonogashira* coupling conditions in the present study improved the yield from 61 to 90%. Similar reaction sequences were used to prepare the geminally bis-functionalized TEEs **6**–**9**. Reaction of **3** with 2 equiv. of *p*-ethynylaniline [21] or *p*-ethynyl-*N*,*N*-didodecylaniline (**5**) afforded bis-donor systems **6** and **8**, respectively, and the conversion with *p*-ethynylnitrobenzene [25] yielded the bis-acceptor system **9**. Alternatively, reaction of **3** with only 1 equiv. of *p*-ethynyl-*N*,*N*-dimethylaniline [26] gave a 1:1 mixture of mono- and bis-donor derivatives **10** and **7**, respectively, which were separated by column chromatography (SiO_2-*H*, hexane/CH_2Cl_2 3:1). Reaction of mono-arylated **10** with *p*-ethynylnitrobenzene then yielded the cross-conjugated donor-acceptor-substituted TEE **11**.

Scheme 1. *Synthesis of Geminally Bis-arylated TEEs* **4**, **6**–**9**, *and* **11**, *and Tetrakis-arylated TEEs* **12**–**15**

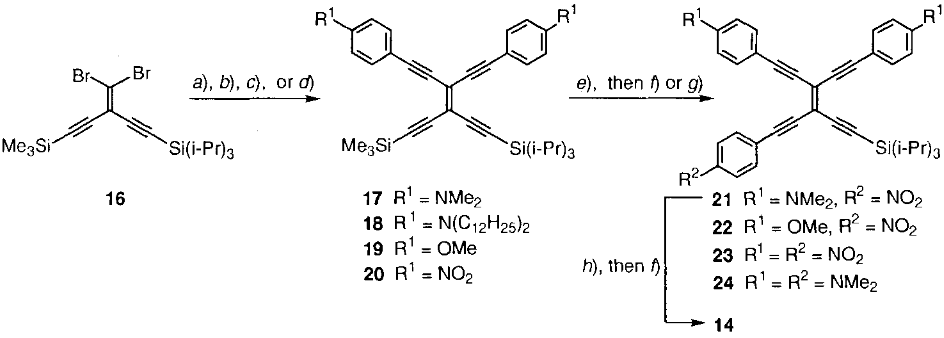


a) *p*-Ethynylaniline, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 24 h; 33% (**6**). *b*) *p*-Ethynyl-*N*,*N*-dimethylaniline (1 equiv.), $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 24 h; 25% (**7**), 21% (**10**). *c*) *p*-Ethynyl-*N*,*N*-didodecylaniline (**5**), $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 48 h; 62% (**8**). *d*) *p*-Ethynylnitrobenzene, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 24 h; 47% (**9**), 25% (**11**). *e*) K_2CO_3, wet MeOH, THF, r.t., 2 h. *f*) Bu_4NF, wet THF, r.t., 0.5 h. *g*) *p*-Iodonitrobenzene, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 18–24 h; 71% (**12**), 26% (**13**), 63% (**14**), 52% (**15**).

The Me$_3$Si groups in **4** were cleanly removed by reaction with K$_2$CO$_3$/MeOH and the (i-Pr)$_3$Si groups in **6**–**8** with Bu$_4$NF to give essentially quantitative yields of the corresponding deprotected TEEs. Removal of the silyl protecting groups was confirmed by IR analysis which showed the disappearance of the strong Si–C stretch at *ca.* 1250 cm^{-1} and the appearance of the ≡C–H stretch at *ca.* 3300 cm^{-1}. Due to limited stability, the deprotected species were quickly used without further characterization. Thus, reaction of deprotected **4**, **6**, and **7** with *p*-iodonitrobenzene gave in good yields the C_{2v}-symmetrical, tetrakis-arylated TEEs **12**–**14**, respectively, which are poorly soluble in all organic solvents. In contrast, tetrakis-arylated TEE **15**, which was obtained by coupling deprotected **8** with *p*-iodonitrobenzene, is a readily soluble compound due to its four dodecyl chains.

The differentially silyl-protected dibromide **16** [6a] was reacted with 2 equiv. of *p*-ethynyl-*N*,*N*-dimethylaniline, *p*-ethynyl-*N*,*N*-didodecylaniline, and *p*-ethynylanisole [27] to give geminally bis-donor-substituted **17**–**19**, respectively, and with *p*-ethynylnitrobenzene to yield the corresponding bis-acceptor derivative **20** (*Scheme 2*). Protodesilylation of **17**, **19**, and **20** (K$_2$CO$_3$, wet MeOH) selectively removed the Me$_3$Si in the presence of the (i-Pr)$_3$Si groups, and the formed terminally deprotected alkynes were directly coupled with *p*-iodonitrobenzene to afford tris-arylated **21**–**23**, and with *p*-iodo-*N*,*N*-dimethylaniline [28] to produce tris-donor-substituted **24**. TBAF-mediated removal of the (i-Pr)$_3$Si group of **21** and coupling with *p*-iodonitrobenzene furnished an alternative route to tetrakis-arylated **14**.

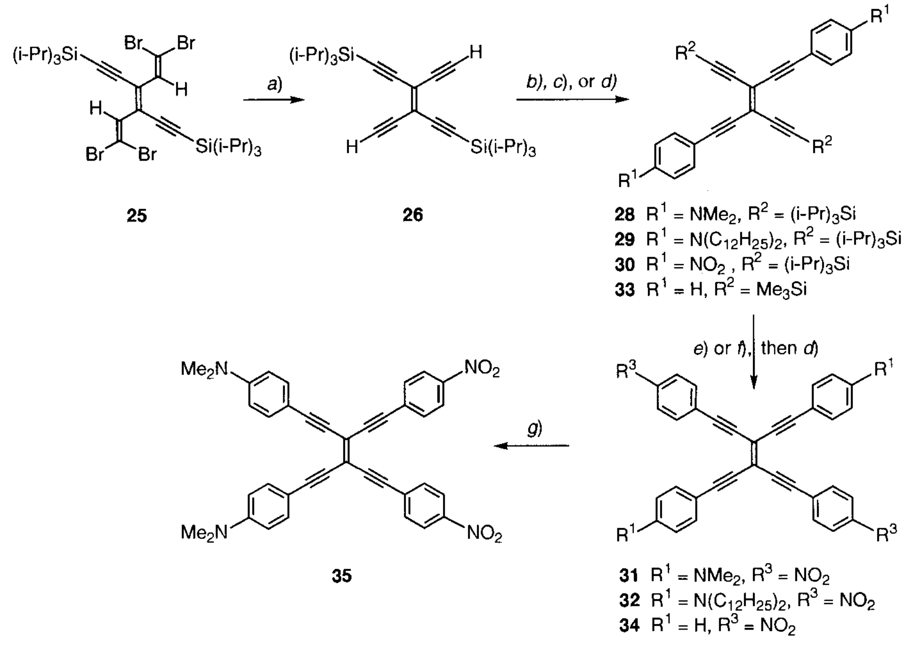
Scheme 2. *Synthesis of Geminally Bis-arylated TEEs* **17**–**20**, *Tris-arylated TEEs* **21**–**24**, *and Tetrakis-arylated* **14**



a) *p*-Ethynyl-*N*,*N*-dimethylaniline, [PdCl$_2$(PPh$_3$)$_2$], CuI, Et$_3$N, r.t., 40 h; 76% (**17**). *b*) *p*-Ethynyl-*N*,*N*-didodecylaniline (**5**), [PdCl$_2$(PPh$_3$)$_2$], CuI, Et$_3$N, r.t., 48 h; 50% (**18**). *c*) *p*-Ethynylanisole, [PdCl$_2$(PPh$_3$)$_2$], CuI, Et$_3$N, r.t., 24 h; 68% (**19**). *d*) *p*-Ethynylnitrobenzene, [PdCl$_2$(PPh$_3$)$_2$], CuI, Et$_3$N, r.t., 72 h; 51% (**20**). *e*) K$_2$CO$_3$, wet MeOH, THF, r.t., 0.5–2 h. *f*) *p*-Iodonitrobenzene, [PdCl$_2$(PPh$_3$)$_2$], CuI, Et$_3$N, r.t., 18–24 h; 79% (**21**), 63% (**22**), 18% (**23**), 70% (**14**). *g*) *p*-Iodo-*N*,*N*-dimethylaniline, [PdCl$_2$(PPh$_3$)$_2$], CuI, Et$_3$N, r.t., 24 h; 19% (**24**). *h*) Bu$_4$NF, wet THF, r.t., 0.5 h.

For the formation of tetrakis-arylated bis-donor/bis-acceptor molecules, the *trans*-bis-deprotected enediyne **26**, prepared from *trans*-tetrabromide **25**, [6a] was smoothly coupled to *p*-iodo-*N*,*N*-dimethylaniline, *p*-iodo-*N*,*N*-didodecylaniline (**27**), or *p*-iodonitrobenzene to give the *trans*-bis-arylated compounds **28**–**30**, respectively. The bis-donor derivatives **28** and **29** were desilylated with TBAF and coupled with *p*-iodonitrobenzene to yield the centrosymmetrical, tetrakis-arylated **31** and **32**, respectively, as black solids. In a similar manner, protodesilylation of diphenyl-substituted TEE **33** [6a] and coupling with *p*-iodonitrobenzene gave the bis-acceptor derivative **34** as a stable, red solid. The synthesis of **35**, the *cis*-isomer of **31**, was then accomplished by photochemical isomerization of **31** in $CHCl_3$ at $\lambda = 366$ nm [29]. Separation of the two isomers was extremely difficult due both to their insolubility as well as their nearly identical polarities. Repeated chromatography, however, afforded small quantities of **35**, thus concluding the series of tetrakis-arylated bis-donor/bis-acceptor molecules which now comprises **13**–**15** (*Scheme 1*) and **31**, **32**, and **35** (*Scheme 3*). These compounds were of particular interest for their enhanced third-order nonlinear optical properties [16a].

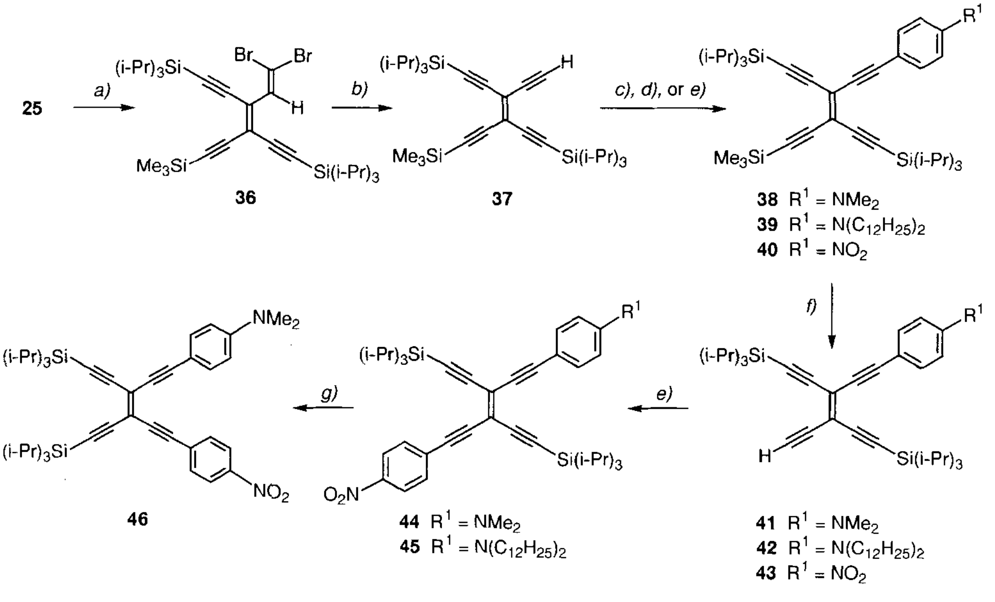
Scheme 3. *Synthesis of* trans-*Bis-arylated TEEs* **28**–**30** *and Tetrakis-arylated TEEs* **31**, **32**, **34**, *and* **35**



a) LDA (6 equiv.), THF, –78°, 30 min, then sat. aq. NH_4Cl soln.; 95%. *b*) *p*-Iodo-*N*,*N*-dimethylaniline, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 24 h; 43% (**28**). *c*) **27**, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 24 h; 28% (**29**). *d*) *p*-Iodonitrobenzene, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 14–24 h; 90% (**30**), 56% (**31**), 34% (**32**), 19% (**34**). *e*) Bu_4NF, wet THF, r.t., 0.5 h. *f*) K_2CO_3, wet MeOH, THF, r.t., 2 h. *g*) *hv* (λ = 366 nm), $CHCl_3$, r.t., 6 h; 20%.

The formation of *trans*-donor-acceptor-substituted TEEs was also of considerable interest, since these molecules provide monomers for the oxidative polymerization leading to laterally functionalized PTAs [14]. Their synthesis proved somewhat more challenging, first requiring transformation of tetrabromide **25** to dibromide **36** and then to mono-deprotected **37** (*Scheme 4*). Thus, **25** was treated with 3 equiv. of LDA, resulting in the formation of the mono-lithium acetylide which was trapped with Me_3SiCl at low temperature to give **36**. Dibromide **36** was then subjected to the LDA-mediated elimination/metallation reaction and subsequently quenched with sat. aqueous NH_4Cl solution to afford TEE **37**. Mono-deprotected **37** was isolated as an unstable solid, though it could be stored for short periods of time at −24° without significant decomposition. Coupling of **37** with *p*-iodo-*N*,*N*-dimethylaniline and *p*-iodo-*N*,*N*-didodecylaniline gave the mono-donor-substituted TEEs **38** and **39**, respectively, whereas coupling with *p*-iodonitrobenzene led to mono-acceptor-substituted **40**. Removal of the Me_3Si protecting group in **38**–**40** gave the terminal alkynes **41**–**43**, respectively. Deprotected TEEs **41** and **43** proved sufficiently stable for full characterization and could be stored under refrigeration at −20° with minimal loss due to decomposition. Conversely, protodesilylation of TEE **39** afforded **42** which was insufficiently stable for isolation and characterization and was thus used without further purification. Subsequent coupling of **41** and **42** with *p*-iodonitrobenzene led to the *trans*-donor-acceptor-substituted chromophores **44** and **45**, which were isolated as a deep-red solid and a deep-red oil, respectively.

Scheme 4. *Synthesis of Mono-arylated TEEs* **38**–**40**, trans-*Donor-Acceptor-Substituted* **44**–**45**, *and* cis-*Donor-Acceptor-Substituted* **46**



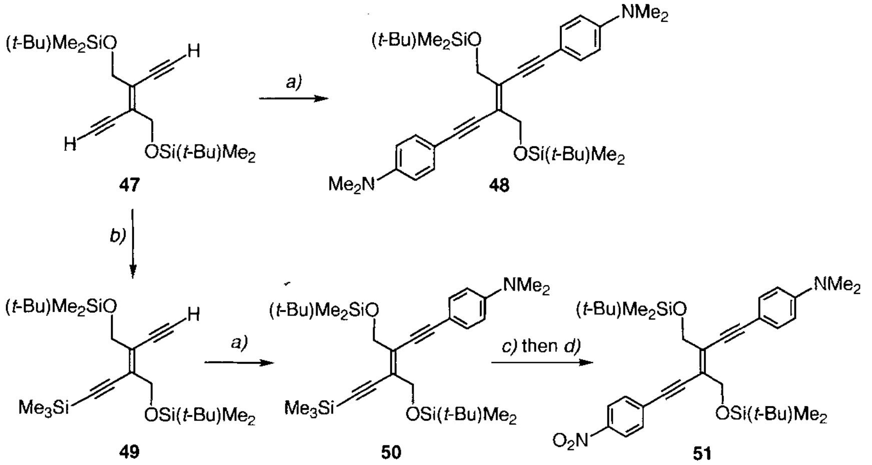
a) LDA (3 equiv.), THF, −78 to −20°, Me_3SiCl, 1 h, then sat. aq. NH_4Cl soln.; 80%. *b*) LDA (3 equiv.), THF, −78 to −20°, 1 h, then sat. aq. NH_4Cl soln.; 91%. *c*) *p*-Iodo-*N*,*N*-dimethylaniline, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 24 h; 50% (**38**). *d*) *p*-Iodo-*N*,*N*-didodecylaniline **27**, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 16 h; 16% (**39**). *e*) *p*-Iodonitrobenzene, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 16–24 h; 80% (**40**), 66% (**44**), 48% (**45**). *f*) K_2CO_3, MeOH, wet THF, r.t., 0.5 h; 99% (**41**), 95% (**43**). *g*) *hν* (λ = 366 nm), Et_2O, r.t., 2 h; 37%.

During the chromatographic purification of **44**, a second, slower running fraction was also isolated and shown to have nearly identical spectral properties to **44**. $^1H\{^1H\}$ Nuclear *Overhauser* effect (NOE) enhancements between the protons *ortho* to the acetylene moieties in the *p*-$O_2NC_6H_4{-}C{\equiv}C$ (7.35 ppm) and *p*-$Me_2NC_6H_4{-}C{\equiv}C$ (7.63 ppm) fragments confirmed the compound to be the *cis*-isomer **46**. Subsequent investigation revealed that monochromatic irradiation at λ = 366 nm of a solution of either **44** or **46** resulted in *cis*/*trans*-isomerization to a **44**/**46** ratio of *ca.* 3:2. Furthermore, the isomerization was found to occur cleanly with no detectable decomposition. Ultimately, the structures of both **44** and **46** were confirmed by single crystal X-ray analyses (*vide infra*) [13].

To investigate the electronic effects of the two pendant, silyl-protected alkynes in the *trans*-bis-arylated TEEs such as **28**, **29**, or **44**, suitable comparison compounds with the pendant alkynes replaced by non-conjugating substituents were desirable. Therefore, bis-arylated (*E*)-hex-3-ene-1,5-diynes with lateral trialkylsilyl-protected methanol substituents were constructed.

trans-Enediyne **47** [11] [30] was coupled with 2 equiv. of *p*-iodo-*N*,*N*-dimethylaniline to give the bis-donor system **48** (*Scheme 5*). The synthesis of a corresponding donor-acceptor-substituted derivative required the preparation of mono-deprotected **49**. Thus, deprotonation of **47** with 1 equiv. of BuLi and quenching with Me_3SiCl provided **49**, which was then coupled with 1 equiv. of *p*-iodo-*N*,*N*-dimethylaniline to give **50**. Selective removal of the Me_3Si group and coupling with *p*-iodonitrobenzene subsequently gave *trans*-donor-acceptor derivative **51** as a stable orange-red solid.

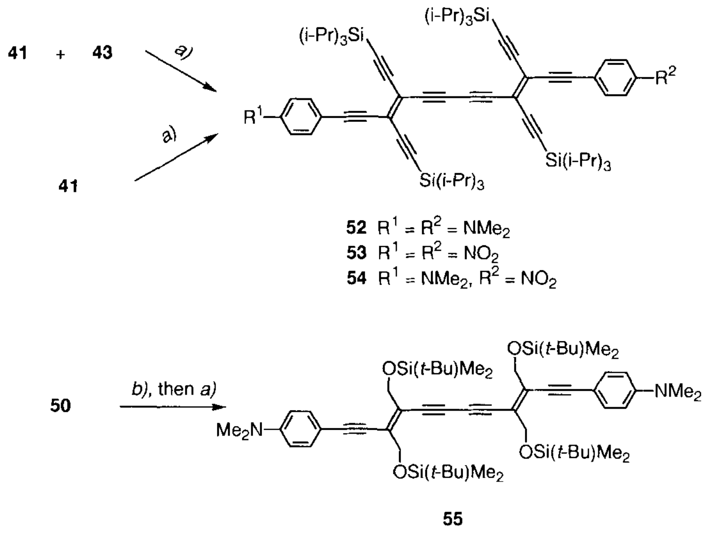
Scheme 5. *Synthesis of Bis-arylated* trans-*Enediynes* **48** *and* **51**



a) *p*-Iodo-*N*,*N*-dimethylaniline, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 24 h; 39% (**48**), 85% (**50**). *b*) BuLi, THF, −78 to −20°, Me_3SiCl, 1 h, then sat. aq. NH_4Cl soln.; 46%. *c*) K_2CO_3, MeOH, wet THF, r.t., 2 h. *d*) *p*-Iodonitrobenzene, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 24 h; 78%.

Investigations of the effects of conjugation length on linear and nonlinear optical as well as electrochemical properties were also of substantial interest [16], and, therefore, a series of donor/acceptor-substituted dimeric TEE derivatives was prepared [9]. Oxidative coupling of a 1:1 mixture of mono-deprotected **41** and **43** under *Hay* conditions [19] [31] provided a statistical ratio (1:1:2) of **52**–**54** in 50% overall yield, from which the pure dimeric compounds were readily isolated by chromatography (SiO_2-*H*, hexane/CH_2Cl_2 1:1) (*Scheme 6*). Alternatively, **52** was also individually synthesized in 53% yield *via* oxidative *Hay* coupling of **41**. For comparison purposes, bis-donor-substituted **55** was prepared as an orange solid by desilylation of **50** followed by oxidative coupling.

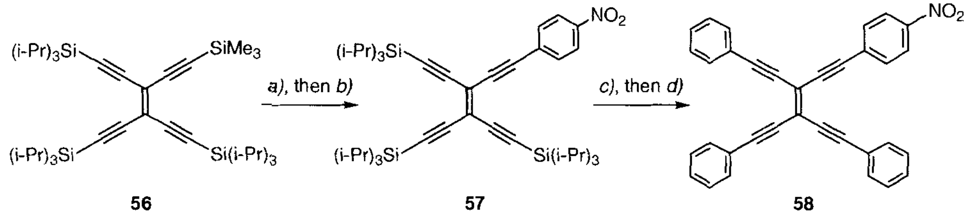
Scheme 6. *Synthesis of Dimeric TEEs* **52**–**54** *and Comparison Compound* **55**



a) CuI, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), O_2, CH_2Cl_2, r.t., 1–2 h; 11% (**52**; 53% from pure **41**), 16% (**53**), 23% (**54**), 63% (**55**). *b*) K_2CO_3, MeOH, wet THF, r.t., 2 h.

For comparison in the electrochemical studies [16c], tetrakis-arylated mono-nitrated **58** was prepared as a red solid, starting from **56** [6a], by Me_3Si group removal, coupling with *p*-iodonitrobenzene to **57**, $(i\text{-}Pr)_3Si$ group removal, and coupling with iodobenzene (*Scheme 7*).

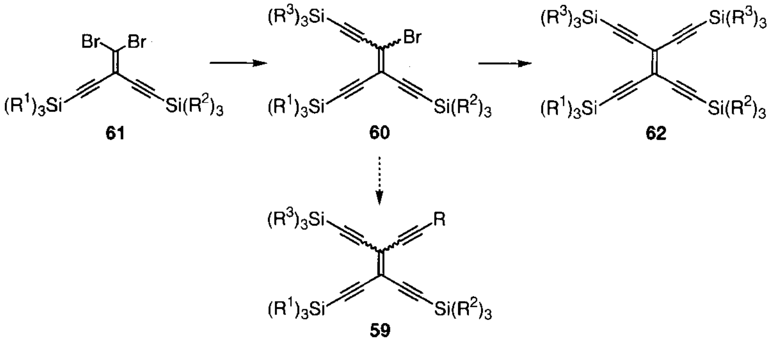
Scheme 7. *Synthesis of Mono-nitrated* **58**



a) K_2CO_3, MeOH, wet THF, r.t., 2 h. *b*) *p*-Iodonitrobenzene, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 18 h; 76%. *c*) Bu_4NF, wet THF, r.t., 0.5 h. *d*) Iodobenzene, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 24 h; 15%.

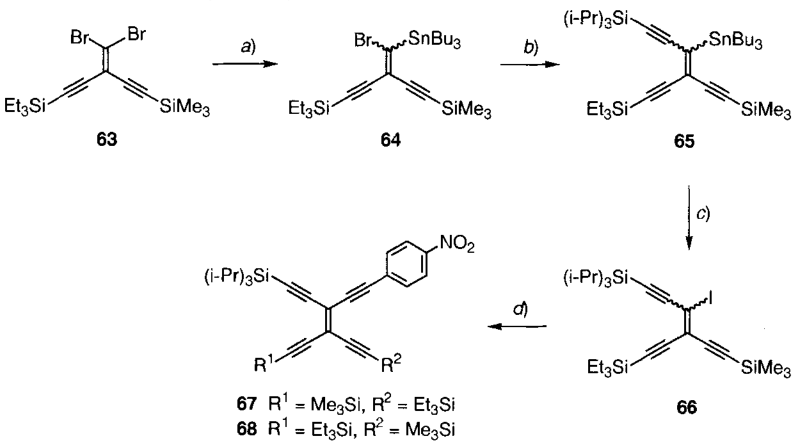
2.3. *Synthesis of TEEs with Four Different Substituents.* The synthesis of differentially tetrasubstituted derivatives such as **59** (*Scheme 8*) is problematic by the usual methods of TEE synthesis. This is mainly due to the fact that (halo)(triethynyl)ethenes of type **60** are not obtainable in good yields, because vinyl bromide **60** is more activated to [Pd]-catalyzed coupling than vinyl dibromide **61**. This ultimately leads to predominant formation of TEE **62** together with only small amounts of **60**. Therefore, a stepwise synthesis for molecules such as **59** and **60** was developed by substituting one of the two Br-atoms in the starting material by a Bu_3Sn group.

Scheme 8. *Potential Synthesis of Differentially Tetrasubstituted TEEs* **59**



Metallation of **63** with BuLi, followed by quenching with Bu_3SnCl gave good yields of compound **64** as a 3:1 mixture of isomers (*Scheme 9*). Although the major isomer could be separated, the coupling reaction toward the synthesis of **65** also resulted in *cis/trans*-isomerization. Hence, **64** was characterized as a mixture of isomers and used as such in subsequent steps. It was soon determined that cross-coupling of vinyl bromides **64** with alkynes in Et_3N resulted in the cleavage of the Bu_3Sn group. Therefore, a more hindered base was chosen and, upon [Pd]-coupling with $(i\text{-}Pr)_2EtN$ in benzene, the two isomers of **65** were obtained in a 3:2 ratio (^1H-NMR) as a yellow oil and in 76% combined yield. Separation and structural assignment of the isomers at this point was impossible due to identical polarities. Treatment of **65** with I_2 in Et_2O [32] readily afforded vinyl iodide **66** in quantitative yields as *ca.* 1:1.1 mixture of isomers (^1H-NMR) which were not separated or assigned. The mixture of **66** was then coupled with *p*-ethynylnitrobenzene under the standard *Sonogashira* conditions to give the differentially tetrakis-substituted TEE isomers **67** and **68** in 70% overall yield in a *ca.* 3:2 ratio. At this stage, isomer separation by column chromatography was finally successful.

Scheme 9. *Synthesis of Differentially Tetrasubstituted TEEs* **67** *and* **68**



a) BuLi, THF, –78°, 1 h, then Bu_3SnCl, –78° to r.t., 16 h; 80%. *b*) Triisopropylsilylacetylene, $[PdCl_2(PPh_3)_2]$, CuI, $(i\text{-}Pr)_2EtN$, benzene, r.t., 4 d; 76%. *c*) I_2, Et_2O, r.t., 14 h; 99%. *d*) *p*-Ethynylnitrobenzene, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 16 h; 42% (**67**), 28% (**68**).

Isomer assignments for **67** and **68** were made on the basis of a single crystal X-ray analysis of **67** (*vide infra*) which showed the Me_3Si group oriented *trans* to the *p*-nitrophenyl moiety. The ability to selectively and sequentially remove the Me_3Si, Et_3Si, and $(i\text{-}Pr)_3Si$ groups is well established [6a] [33]. Hence, TEEs such as **87** and **68** represent valuable building blocks for the synthesis of differentially tetra-functionalized TEEs *via* stepwise deprotection-coupling sequences.

2.4. *Stability of Arylated TEEs.* The thermal stability of a representative group of the arylated TEEs was examined by both conventional melting-point (m.p.) determination and differential scanning calorimetry (DSC). The melting/decomposition point (m.p./d.p.) data are summarized in *Table 1*. Though both m.p. and DSC values may vary slightly dependent upon the rate of heating, a comparison of the results obtained by both methods shows them to generally be in good agreement.

Table 1. *Melting- and Decomposition-Point Data for Arylated Tetraethynylethenes*

Compound	M.p. [°C]	DSC Measurements	
		M.p. [°C]	D.p. [°C]
7	155–156	160	270
9	167	174	205
11	129–130	129	210
12	168 (dec.)	[a])	160
14	247 (dec.)	[a])	240
21	169–170 (dec.)	163	165
28	217–218	219	240
30	225–226 (dec.)	[a])	220
31	255 (dec.)	[a])	230
34	205–210 (dec.)	[a])	200
44	190–191 (dec.)	181	190

[a]) No observed melting point.

The arylated TEEs investigated in this study exhibited remarkably high thermal stability: all decomposed at temperatures higher than 160°, and many were stable well over 200°. With the exception of **30**, bis-arylated TEEs showed defined melting points before the onset of decomposition. As the degree of arylation increased to the tris- and tetrakis-arylated derivatives, however, decomposition became dominant. For example, whereas tris-arylated **21** showed a m.p. of 163°, decomposition rapidly followed at 165°, and though tetrakis-arylated TEEs **14** and **31** were stable to 240 and 230°, respectively, only decomposition points were observed for these molecules.

For bis-arylated TEEs, thermal stability was anticipated to depend on the orientation of the aryl rings. *Alberts* had found that linearly-conjugated *trans*-1,6-bis(trimethylsilyl)hex-3-ene-1,5-diyne was more stable than the cross-conjugated isomer, 1,5-bis(trimethylsilyl)-3-methylidenepenta-1,4-diyne [34]. In the case of the studied TEEs, however, a similar trend was not observed. Whereas geminally bis-acceptor-substituted TEE **9** (d.p. $\approx 205°$) is slightly less stable than the corresponding *trans*-derivative **30** (d.p. $\approx 220°$), both the geminally donor-acceptor and geminally bis-donor-substituted TEEs **11** and **7** are more stable than their linearly-conjugated *trans*-analogs **44** and **28**, respectively. Though as stable or more stable than their *trans*-analogs, all geminally bis-arylated TEEs studied (**7**, **9**, and **11**) exhibited melting points at temperatures considerably below their decomposition points. This is likely due to the inability of these molecules to adequately orient their proximate bulky $(i\text{-Pr})_3Si$ groups in a manner favorable to crystal packing. This steric obstacle to the formation of stable crystal lattices is also evidenced by the inability to grow high-quality crystals for X-ray analysis of any geminally functionalized derivative despite exhaustive attempts, whereas the *trans*-analogs afforded X-ray-quality crystals much more readily (*vide infra*).

Only one of the molecules investigated by DSC showed a phase transition preceding melting or decomposition. Bis-donor-substituted **28** underwent a phase transition at *ca.* 173° (*Fig. 2*). The relevance of this phase transition to the polymorphism exhibited by **28** as determined by X-ray crystallography (*vide infra*) is at present undetermined.

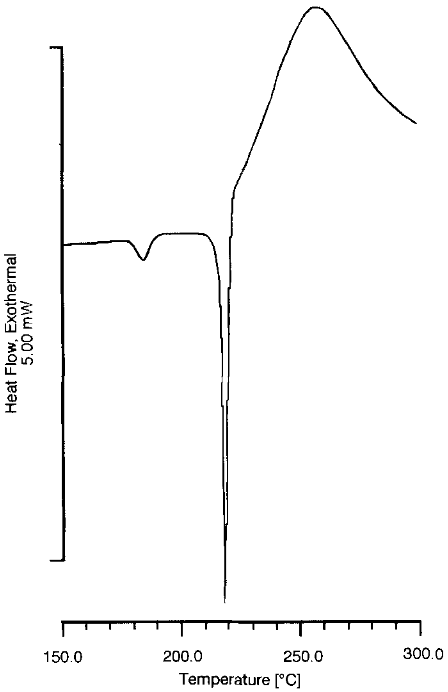


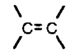
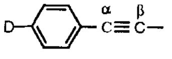
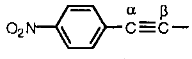
Fig. 2. *Differential scanning calorimetry spectrum for* **28** (heating rate = 10 K min^{-1})

The majority of arylated TEEs are photochemically stable, but molecules **30**, **31**, **35**, **44**, and **46** were observed to slowly undergo *cis/trans*-isomerization in solution when exposed to UV light. In the pure crystalline state, however, all solid compounds were stable to moisture, air, and light, and remained unchanged for months on a laboratory bench.

In contrast to the crystalline p-$Me_2NC_6H_4$-substituted TEEs, the derivatives bearing p-$(C_{12}H_{25})_2NC_6H_4$ moieties were either isolated as oils (**8**, **18**, **29**, **39**, and **45**) or as an oily solid (**15**). As the only exception, tetrakis-arylated **32** formed a microcrystalline solid. In many cases, the stability of the p-$(C_{12}H_{25})_2NC_6H_4$ derivatives is lower than that of their p-$Me_2NC_6H_4$ counterparts. In particular, bis-arylated **8**, **18**, and **45** tend to slowly decompose over a period of weeks, even when kept under refrigeration. On the other hand, the tetrakis-arylated derivatives **15** and **32** remained unchanged for weeks at room temperature or for years under refrigeration.

2.5. *^{13}C-NMR Analysis of Donor/Acceptor-Substituted TEEs.* In the ^{13}C-NMR spectra of arylated TEEs, the acetylenic resonances of residual $R_3Si-C{\equiv}C$ moieties appear in a narrow range between 100 and 104 ppm, regardless of the presence of donor and/or acceptor groups on the aromatic rings. In contrast, the positions of the acetylenic and central olefinic C-atoms of the TEE core are quite diagnostic (*Table 2*). The acetylenic resonances in donor (D)-substituted p-$D-C_6H_4-C(\alpha){\equiv}C(\beta)$ fragments shift little as the degree and pattern of the TEE substitution are altered. Thus, with Me_2N-substituents on the aryl ring, resonances of $C(\alpha)$ at 86–87 ppm and of $C(\beta)$ at 103–105 ppm were observed, whereas in the presence of MeO-substituents the signals of $C(\alpha)$ appeared at 86–87 ppm and those of $C(\beta)$ at 99–100 ppm. As a comparison, the corresponding resonances in the $Ph-C{\equiv}C$ fragments of **33** appear at 87 ($C(\alpha)$) and 99 ($C(\beta)$) ppm [6a]. Likewise, the acetylenic resonances in p-$O_2N-C_6H_4-C(\alpha){\equiv}C(\beta)$ fragments were also little effected by the presence of other functionality and appeared at 95–96 ($C(\alpha)$) and 91–94 ($C(\beta)$) ppm.

Table 2. *Selected ^{13}C-NMR Data for Arylated Tetraethynylethenes*[a])

Compound					
		C(α)	C(β)	C(α)	C(β)
7	113, 119	87[b])	105[b])		
9	115, 121			96	91
11	116, 117	86[b])	[c])	95	92
14	110, 123	87[b])	104[b])	96	93
17	113, 120	86, 87[b])	103, 104[b])		
19	116, 119	86, 87[d])	99, 99[d])		
21	111, 121	87, 87[b])	[c])	95	94
22	114, 120	86, 87[d])	100, 100[d])	95	93
28	115	87[b])	104[b])		
30	118			96	92
31	116	86[b])	103[b])	96	93
33[f])	118	87[e])	99[e])		
35	116	87[b])	103[b])	96	93
38	115, 119	87[b])	104[b])		
40	117, 119			95	92
44	113, 120	87[b])	[c])	95	93
46	113, 120	87[b])	[c])	95	94
56	117, 117				

[a]) Measurements in $CDCl_3$, reported in ppm. [b]) $D = Me_2N$. [c]) Not assignable. [d]) $D = MeO$. [e]) $D = H$. [f]) [6a].

In contrast to the acetylenic ^{13}C-resonances, those of the central olefinic C-atoms experienced more significant changes in chemical shift as a function of degree and nature of aryl substitution. Persilylated TEEs such as **56** display resonances at 117 ppm for the $C(sp^2)$-atoms, similar to that of diphenyl derivative **33** (118 ppm). Addition of a p-$O_2NC_6H_4$ group as in **40** (117 and 119 ppm) or a p-$Me_2NC_6H_4$ group as in **38** (115 and 119 ppm), or the incorporation of both as in the cross-conjugated donor-acceptor-system

11 (116 and 117 ppm) causes only a slight shift of the C(sp^2)-atom resonances. In the series of donor-acceptor-substituted TEEs with linear conjugation, however, steady changes in position of the olefinic resonances are observed as the degree of aryl substitution is increased from **44** and **46** (113 and 120 ppm), to **21** (111 and 121 ppm), and finally to **14** (110 and 123 ppm). It remains unclear at present, why the resonances of the central olefinic C-atoms in the TEE frame are more sensitive to the nature and degree of aryl substitution than the adjacent acetylenic resonances.

2.6. *Electronic Absorption Spectra of Donor/Acceptor-Substituted TEEs.* The UV/VIS spectra of the arylated TEEs (*Table 3*) provided a great deal of information about their electronic structures. For comparison, it was helpful that variance of the R_3Si alkyne-protecting groups had only a minimal effect on the spectra as shown for the longest-wavelength band (λ_{max} [nm], ε [M^{-1} cm^{-1}]) in the series of *p*-$O_2NC_6H_4$ derivatives **40** (382, 26500), **57** (383, 24200), **67** (382, 24900), and **68** (383, 25800). In the following, the position of the longest-wavelength absorption band is investigated as a function of the nature and orientation of the aryl substituents in $CHCl_3$.

In the series of donor-substituted derivatives, a large bathochromic shift was observed in the spectrum of *trans*-bis-$Me_2NC_6H_4$-substituted TEE **28** (λ_{max} = 459 nm, *Table 3*) as compared to that of its geminally oriented counterpart **7** (λ_{max} = 428 nm). In the series of bis-nitrophenyl derivatives too, *trans*-substituted **30** (λ_{max} = 403 nm) displayed a longer-wavelength absorption than the corresponding geminally substituted **9** (λ_{max} = 388 nm). The spectra of all donor-acceptor-substituted molecules exhibited broad absorption bands at lower energy with end-absorptions extending beyond 550 nm. These bands are characteristic for intramolecular charge-transfer (CT) transitions. Large ε values suggest that the intramolecular donor-acceptor interactions are very efficient. The magnitude of the donor-acceptor conjugation, as approximated by the position of the CT band, is significantly weaker in the geminal donor-acceptor system **11** (λ_{max} = 447 nm) than in the corresponding *cis*- (**46**, λ_{max} = 471 nm) and *trans*-derivatives (**44**, λ_{max} = 468 nm). All of these comparisons between geminally and *cis*/*trans*-diarylated TEE demonstrate that cross-conjugation paths are less efficient than linear conjugation paths [9a] [10].

The addition of a second electron-donating group in tris-arylated **21** had little effect on shape or position of the CT band which appeared at a position (λ_{max} = 461 nm) similar to that seen in the spectrum of the *trans*-donor-acceptor system **44** (*Fig. 3*). In tetrakis-arylated TEE **14**, two *trans*-donor-acceptor conjugation paths are effective. In comparison to **21** and **44** with only one such conjugation path, the CT band of **14** appears at lower energy (λ_{max} = 486 nm), is broader with an end-absorption much above 600 nm, and has a higher intensity (*Fig. 3*). Similar differences were observed when the CT band of **46**, with one *cis*-donor-acceptor conjugation path, was compared to tetrakis-arylated **31** with two such linear conjugation paths. Increasing the linear conjugation length also produced a bathochromic shift of the CT band as revealed by the comparison of monomeric TEE **44** (λ_{max} = 468 nm) to dimeric **54** (λ_{max} = 481 nm).

Quite unexpectedly, *N*-substitution in the $R_2NC_6H_4$ donor groups strongly influenced the position of the CT band in donor-acceptor systems such as the tetrakis-arylated molecules **13**–**15** (*Fig. 4*). As the *N*-substitution progresses from H to Me and finally to $C_{12}H_{25}$, λ_{max} increases from 471, to 486, and to 511 nm. In addition, the molar extinction coefficients also increase in the same trend, almost doubling from 22800 M^{-1} cm^{-1} (**13**) to a value of 44600 M^{-1} cm^{-1} (**15**).

Table 3. *Maxima of the Longest-Wavelength Absorptions* λ_{max} [nm] *and Molar Extinction Coefficients* (ε)[a] *of Arylated Tetraethynylethenes*

Compound	Solvent				
	Hexane	Et_2O	C_6H_6	$CHCl_3$	Acetone
4				377 (31500)	
6				428 (45100)	
7	428 (51400)	423 (56300)	433 (55300)	428 (51100)	435 (54200)
8				443 (52100)	
9	397 (38700)[b]	387 (37500)	394 (33200)	388 (33200)	386 (36200)
10	416 (41700)			420 (38000)	
11	442 (34000)	446 (23100)	456 (16100)	447 (19900)	456 (19400)
12				426 (36000)	
13				471 (22800)	
14	[c]	474 (40100)	488 (39800)	486 (40700)	488 (44300)
15				511 (44600)	
17				430 (52700)	
19	386 (31200)	387 (36100)	394 (35000)	375 (36200)[d]	375 (38900)[e]
20				387 (33400)	
21	441 (39300)	449 (42700)	460 (41900)	461 (38200)	463 (43000)
22	415 (29600)	412 (29200)	415 (28200)	428 (28900)	413 (31400)
23				403 (35100)	
24	455 (48800)	462 (45100)	471 (43100)	471 (44300)	476 (46800)
28	452 (47200)	457 (46100)	461 (43900)	459 (41000)	469 (43200)
29				478 (55200)	
30	416 (30300)[f]	390 (34200)	395 (31200)	403 (34000)	390 (33400)
31				533 (22000)	
32				556 (24700)	
34				427 (29900)	
35				520 (23800)	
38	429 (29700)			433 (29300)	
39				448 (32100)	
40	396 (26200)[g]			382 (26500)	
44	453 (36600)	458 (31600)	465 (27300)	468 (31200)	469 (33200)
45				488 (25700)	
46				471 (17000)	
48				397 (51400)	
50				366 (35700)	
51				424 (25000)	
52	464 (29300)			486 (45100)	
53				456 (41600)	
54				481 (31300)	
55				416 (68300)	
57				383 (24200)	
58				418 (22100)	
67				382 (24900)	
68				383 (25800)	

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[a] $[\mathrm{M}^{-1}\,\mathrm{cm}^{-1}]$. [b] Absorption band not visible in other solvents. The band in hexane at 387 nm (ε 38600) provides accurate comparison to λ_{max} in other solvents. [c] Not recorded due to insolubility. [d] Shoulder at 394 nm (ε 34500). [e] Shoulder at 395 nm (ε 36100). [f] Absorption band not visible in other solvents. The band in hexane at 396 nm (ε 38600) provides accurate comparison to λ_{max} in other solvents. [g] Absorption band not visible in other solvents. The band in hexane at 377 nm (ε 29800) provides accurate comparison to λ_{max} of $CHCl_3$.

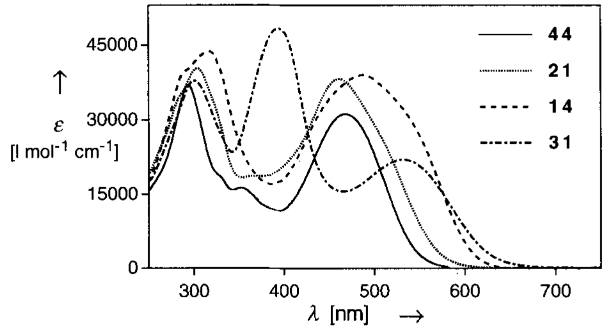

Fig. 3. *Electronic absorption spectra in $CHCl_3$ comparing the effects of donor-acceptor-substitution for* **44**, **21**, **14**, *and* **31**

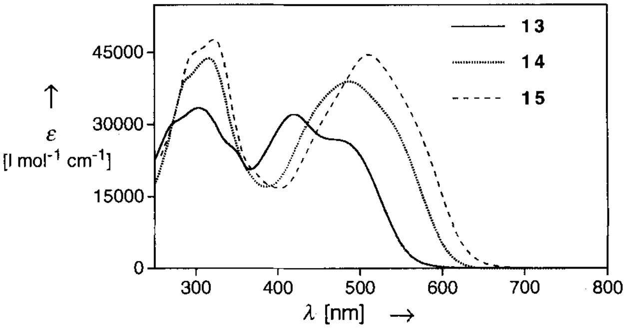

Fig. 4. *Electronic absorption spectra in $CHCl_3$ comparing the effects of* N*-substitution in donor-acceptor functionalized* **13**, **14**, *and* **15**

Protonation of the $R_2NC_6H_4$ group in donor-acceptor-substituted molecules by treatment with conc. aqueous HCl resulted in complete loss of the CT transitions and afforded spectra with longest-wavelength maxima around $\lambda_{max} \approx 380$ nm, typical of Ph or *p*-$O_2NC_6H_4$-substituted TEEs. The quenching of the CT absorptions by protonation is reversible: treatment of the protonated forms with aqueous NaOH regenerated the neutral species, and the UV/VIS spectra became virtually identical to those measured before the acidic treatment. This is shown in *Fig. 5, a*, for the *cis*-donor-acceptor-substituted TEE **46**. Higher-energy transitions in the spectra were only slightly affected by the addition of the acid.

The spectra of bis-donor substituted TEEs such as **7** and **28** were also strongly affected by the addition of conc. aqueous HCl. Upon protonation, the lower-energy absorption in geminally bis-donor-substituted **7** appeared at higher energy and the overall spectrum now very much resembled that of the geminally substituted diphenyl derivative **4** (*Fig. 5, b*).

Pendant $R_3Si{-}C{\equiv}C$ groups cause a significant bathochromic shift of the longest-wavelength absorption band in substituted TEEs. This is clearly revealed by the comparison between *trans*-donor-acceptor-substituted TEE **44** and the corresponding *trans*-enediyne **51** (*Fig. 6, a*) as well as between the dimeric bis-donor TEE derivative **52** and the

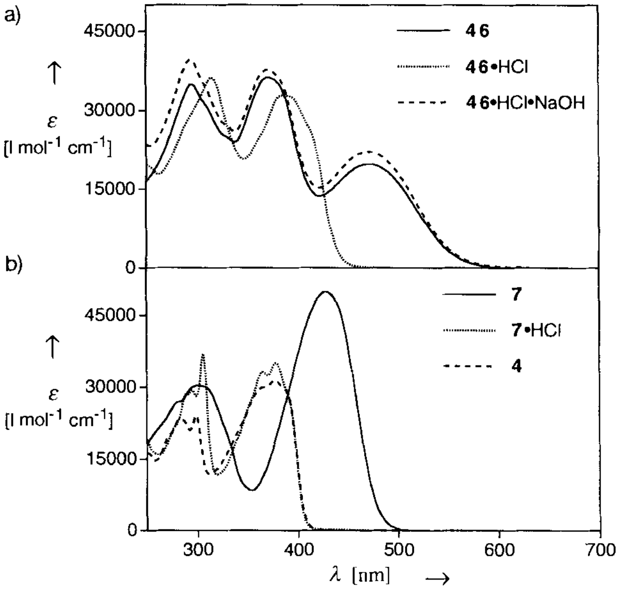

Fig. 5. *Effects of protonation on the electronic absorption spectra in* $CHCl_3$ *of* a) cis-*donor-acceptor-substituted TEE* **46** *and* b) *geminally bis-donor-substituted* **7** *in comparison to the geminal diphenyl derivative* **4**. Addition of NaOH to the protonated species regenerates the original spectrum.

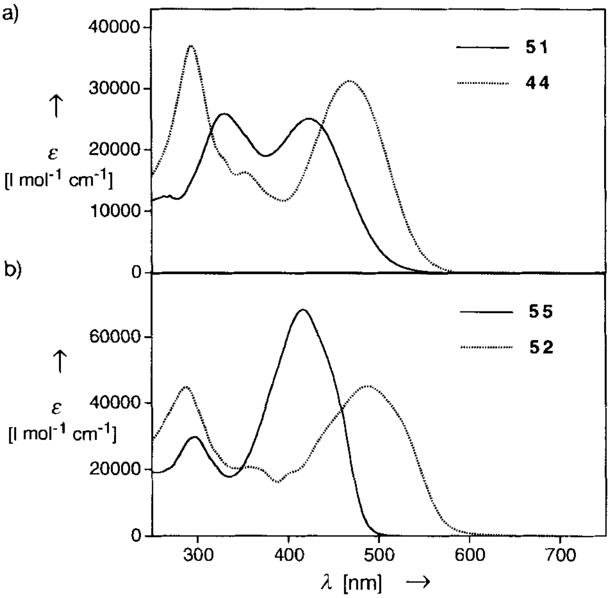

Fig. 6. *Electronic absorption spectra in* $CHCl_3$ *showing the effects of the pendant* $R_3Si-C{\equiv}C$ *groups in TEEs by comparison of* a) *TEE* **44** *to enediyne* **51** *and* b) *dimeric TEE* **52** *to dodeca-3,9-diene-1,5,7,11-tetrayne* **55**

bis-donor-substituted dodeca-3,9-diene-1,5,7,11-tetrayne **55** (*Fig. 6,b*). The longest-wavelength band of **51** (λ_{max} = 424 nm) appears 44 nm higher in energy than the corresponding band of **44**. Likewise, the lowest-energy absorption of **55** (λ_{max} = 416 nm) appears 70 nm higher in energy relative to the corresponding, weaker band of **52**. These comparisons suggest a substantial participation of the pendant $R_3Si-C\equiv C$ groups in the overall π-electron delocalization in donor/acceptor substituted TEEs.

The number, nature, and orientation of substituents all affect the solvatochromism observed for the electronic transitions in TEE derivatives. For example, the longest-wavelength absorption of the bis-acceptor derivatives **9** and **30** at $\lambda_{max} \approx 390$ nm was nearly solvent independent, whereas the corresponding band in the bis-donor molecules **7** and **28** showed slight bathochromic shifts with increasing solvent polarity (*Table 3*). The CT bands of the donor-acceptor systems **11** and **44** also displayed a modest solvatochromism, in agreement with an increase in dipole moment from the ground to the excited states. Interestingly, the tris-arylated derivatives **21** and **24** exhibited a much stronger solvatochromism than the bis-arylated counterparts (*Table 3*); a comparison to the tetrakis-arylated derivatives was not possible due to their limited solubility in apolar solvents.

2.7. *Fluorescence Spectroscopy of Donor/Acceptor-Substituted TEEs.* A majority of the compounds examined showed strong fluorescence emission in solution (*Table 4*). The emission for the geminally and *trans*-donor-acceptor-substituted TEEs **11** and **44** displayed a dramatic solvent dependency, which reflects the existence of highly polarized excited states in these molecules [35]. Whereas no emission was observed in $CHCl_3$, a weak fluorescence was recorded in Et_2O (λ_{em} = 600 (**11**) and 605 (**44**) nm) and a strong one in hexane (λ_{em} = 522 (**11**) and 536 (**44**) nm). No fluorescence was detected for compounds with three (**21**) or four donor/acceptor groups (*i.e.*, **14**, **31**, or **35**), or for the dimeric donor-acceptor compound **54**.

Solvent effects on fluorescence emission were much less pronounced for bis-donor-substituted molecules such as **7** or **28**, or tris-donor-functionalized **24**. For example, geminally disubstituted TEE **7** showed strong emissions in $CHCl_3$ (λ_{em} = 519 nm), Et_2O (λ_{em} = 514 nm), benzene (λ_{em} = 506 nm), and hexane (λ_{em} = 478 nm). Tris-donor-substituted **24** displayed even less solvatochromism with the emission maxima in $CHCl_3$ (λ_{em} = 525 nm), benzene (λ_{em} = 514 nm), hexane (λ_{em} = 510 nm), and Et_2O (λ_{em} = 506 nm) appearing within a narrow span of only 19 nm.

Whereas a strong fluorescence was recorded in $CHCl_3$ for the acceptor-substituted **30**, **40**, and **53** (λ_{em} = 494, 519, and 504 nm, resp.), these compounds did not give any emission in Et_2O or hexane.

2.8. *X-Ray Crystal-Structure Analyses of Donor/Acceptor-Substituted TEEs.* Prior to this study, several X-ray crystal structures of R_3Si- and Ph-substituted TEEs had been published [5a] [6] [9] [10] [12]. They consistently showed fully planar conjugated C-skeletons including Ph rings without *o*- or *m*-substituents. To explore possible structural effects of donor/acceptor-substitution on the bonding, X-ray structural analyses were performed during the course of this investigation for compounds **30**, **44**, **46**, **48**, **67**, and for two polymorphic forms of **28**. The molecular structures of **44**, **46**, **48**, and one modification of **28** had been described in [13]; therefore, the discussion of the structural properties of these compounds will only be brief here.

Table 4. *Fluorescence Data for Arylated Tetraethynylethenes*

Compound	Solvent	$\lambda_{em,max}$ [nm]	λ_{ex} [nm]	$\varepsilon(\lambda_{ex})$ [M^{-1} cm^{-1}]	Φ_F[a])
7	$CHCl_3$	519	430	51100	0.15
	Benzene	506	430	55300	0.20
	Et_2O	514	430	54600	0.15
	Hexane	478	400	50500	0.24
11	Et_2O	600	450	22900	0.02
	Hexane	522	400	19700	0.63
19	$CHCl_3$	433	370	35600	0.25
22	$CHCl_3$	597	440	28900	0.38
24	$CHCl_3$	525	430	44600	0.30
	Benzene	514	430	45900	0.22
	Et_2O	506	430	45300	0.31
	Hexane	510	400	31400	0.46
28	$CHCl_3$	522	440	34600	0.43
	Benzene	512	430	34700	0.32
	Et_2O	509	430	38900	0.19
	Hexane	502	400	26500	0.53
30	$CHCl_3$	494	400	33900	0.30
38	$CHCl_3$	526	430	29200	0.57
	Hexane	454	400	24100	0.39
40	$CHCl_3$	519	400	22400	0.66
44	Et_2O	605	450	30900	0.01
	Hexane	536	400	14800	0.42
48	$CHCl_3$	439	350	34700	0.29
51	Hexane	480	400	17500	0.13
52	$CHCl_3$	588	480	44400	0.15
53	$CHCl_3$	504	455	41900	0.17
55	$CHCl_3$	505	450	47800	0.22

[a]) Fluorescence quantum yield [35].

The molecular structures of donor-acceptor-substituted **44** and **46** showed little indication of an intramolecular ground-state charge-transfer, and bond lengths and angles of their TEE cores were in the range of those seen in the previously studied derivatives [13]. These findings are in good agreement with similar and independent investigations by *Brédas* and coworkers [36], and *Stiegman* and coworkers [37] on donor-acceptor-substituted α,ω-diphenylpolyynes, which showed little distortion of the C–C and C≡C bonds linking the donor and acceptor moieties. The entire conjugated C-frames in **44** and **46** are nearly perfectly planar with the aryl rings rotated less than 3° out of the best plane through the TEE cores. In contrast, the aryl rings of the p-$Me_2NC_6H_4$ moieties in **48** are rotated by *ca.* 11° out of the best plane of the central enediyne core, presumably due to crystal packing effects.

Following a first X-ray crystal-structure analysis of **28** ('structure 1'), which revealed a triclinic space group ($P\bar{1}$) [13], a second, different structure ('structure 2') with the same space group was solved. The major differences between the two structures result from the number of molecules in the unit cell as well as from the relative orientations of adjacent molecules. Crystals grown at room temperature by slow diffusion of hexane into a solution of **28** in CH_2Cl_2 provided the previously reported 'structure 1' [13]. This structure showed one centrosymmetric molecule in the unit cell, and the $Me_2NC_6H_4$ moieties were rotated by *ca.* 29° out of the best plane of the TEE core. The analysis of the crystal packing revealed a basically linear alignment of the $Me_2NC_6H_4$-substituted enediyne portions of the molecules (*Fig. 7*). The TEE C-cores of neighboring molecules are fully isolated by the $(i\text{-}Pr)_3Si$ groups; thus the most reactive portions of neighboring molecules are effectively prevented from contact and interaction. This 'insulating effect' is a strong, recurring motif in solid state structures of $(i\text{-}Pr)_3Si$-substituted TEEs and accounts for much of their thermal stability [6a] [9] [10] [38].

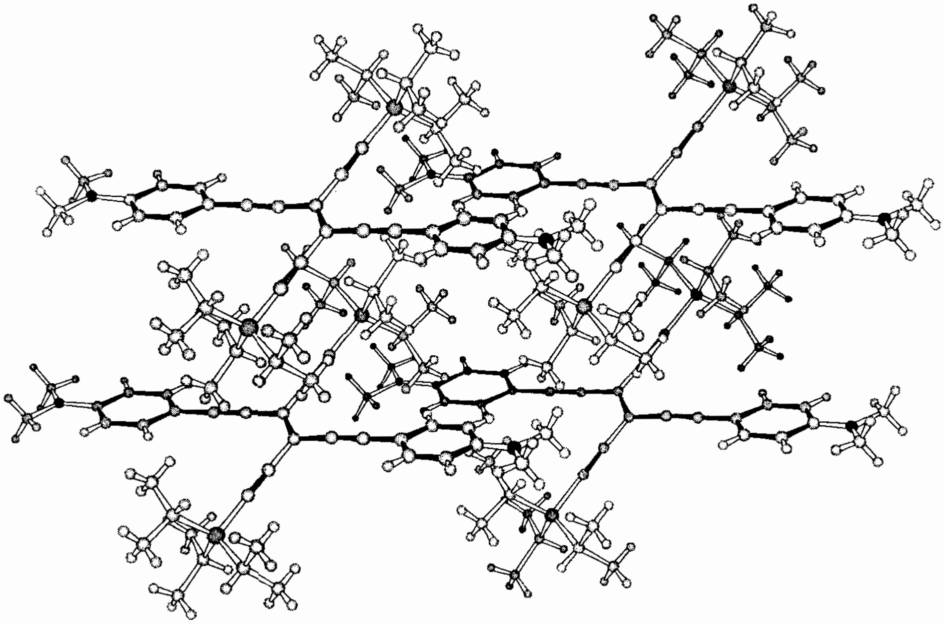

Fig. 7. *Crystal packing for 'structure 1' of* **28** *showing the linear alignment of the* $Me_2NC_6H_4$*-substituted enediyne moieties*

Crystals grown at 0° by slow diffusion of hexane into a solution of **28** in CH_2Cl_2 provided 'structure 2'. The unit cell of this structure contained two crystallographic different, centrosymmetrical molecules in an orthogonal orientation with respect to one another. Bond lengths and angles of **28** in both 'structure 1' and 'structure 2' are very similar (*Fig. 8*) [13]. Again, the analysis of the crystal packing showed the efficient separation of the TEE cores of neighboring molecules by sheets of $(i\text{-}Pr)_3Si$ groups.

Slow evaporation of a solution of **30** in MeCN provided crystals suitable for X-ray diffraction. Unfortunately, large disorder in the $(i\text{-}Pr)_3Si$ groups precluded refinement of the X-ray crystal structure to a level that would provide bond lengths and angles sufficiently accurate for meaningful comparisons. Analysis of the crystal packing of **30** (*Fig. 9*) showed that the $O_2NC_6H_4$ moieties are rotated by almost 90° out of the best plane through the central TEE core. This orthogonal arrangement is likely due to crystal packing effects and maintains π-electron conjugation between each nitroaryl ring and

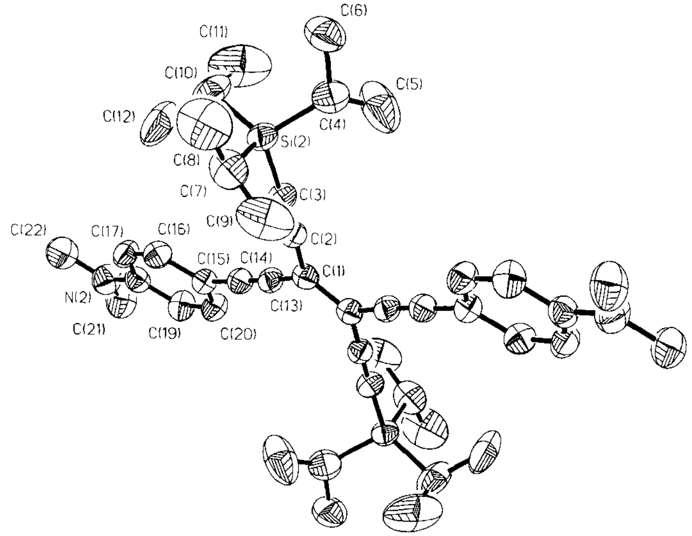

Fig. 8. *X-Ray crystal structure of* **28** *in 'structure 2'.* Shown is one of the two crystallographically different molecules in the unit cell. Selected bond lengths [Å] and angles [°]: C(15)–C(14) 1.438(11), C(14)–C(13) 1.209(12), C(13)–C(1) 1.388(10), C(1)–C(2) 1.449(11), C(2)–C(3) 1.198(11), C(3)–Si(2) 1.823(9), C(1)–C(1A) 1.392(13); C(15)–C(14)–C(13) 178.4(8), C(14)–C(13)–C(1) 176.5(8), C(13)–C(1)–C(2) 117.7(6), C(1)–C(2)–C(3) 177.0(7), C(2)–C(3)–Si(2) 179.1(5), C(13)–C(1)–C(1A) 122.7(9), C(1A)–C(1)–C(2) 119.5(8).

one adjacent set of acetylenic π-orbitals [12a] [39]. The molecules are arranged in columnar stacks, and the stacks are aligned into sheets along the axis through the *trans*-diarylated enediyne moities. The (i-Pr)$_3$Si groups both separate adjacent sheets and interlock with each other to afford the cohesive forces holding the crystal together.

Single crystals of **67** suitable for X-ray analysis were grown at room temperature by slow diffusion of hexane into CH_2Cl_2. As observed for other TEEs containing different R_3Si groups, the structure of **67** was highly disordered, in particular in the regions of the silyl groups. In contrast to **30**, it shows a location of the $O_2NC_6H_4$ substituent in plane with the central TEE C-core. This structure was essential in the assignment of the isomeric configurations of **67** and **68** (*Sect. 2.3*).

3. Conclusions. – A large series of structurally related, conjugated, donor- and/or acceptor-functionalized molecules based on the tetraethynylethene (TEE) C-skeleton was prepared by [Pd]-catalyzed cross-coupling reactions. The *Sonogashira* coupling conditions were found as the most practical and highest-yielding in the construction of the targeted compounds from terminally alkyne-deprotected TEEs and the corresponding p-substituted aryl halides (p-Y–C_6H_4–X; X = Br or I; Y = R_2N, O_2N, MeO, H). Melting-point determinations and differential scanning calorimetry demonstrated a remarkable stability of these compounds, which mostly melt or decompose only above 200°. X-Ray structure analyses of *cis*- and *trans*-donor-acceptor-substituted TEEs showed the molecules to be essentially planar with normal bond lengths and angles, supporting the contention that little intramolecular charge-transfer is contributing to the electronic ground state. The UV/VIS spectra of donor-acceptor TEEs all displayed broad, intensive

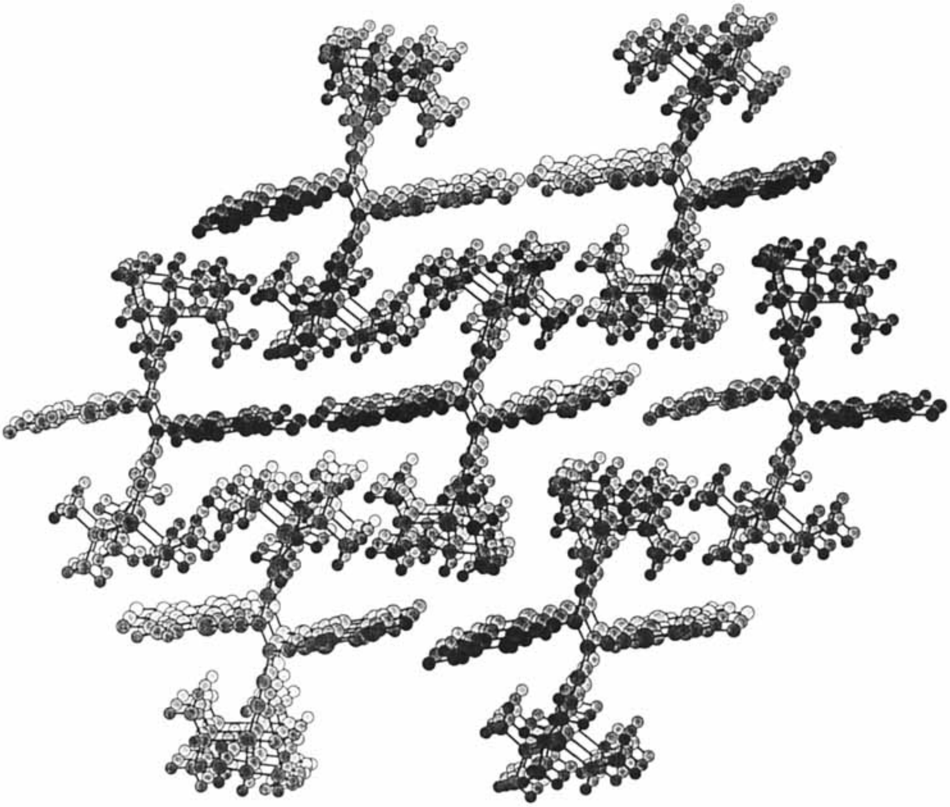

Fig. 9. *Crystal packing of* trans-*bis-acceptor-substituted* **30** *showing the perpendicular orientation of the nitrophenyl moieties with respect to the adjacent TEE core.* Columnar stacks of **30** are aligned within sheets separated by the (i-Pr)$_3$Si groups.

low-energy absorptions attributable to considerable polarization from the donor to the acceptor moieties in the excited state. The electronic absorption spectra provided strong evidence that charge delocalization along linear conjugation paths in *cis*- and *trans*-donor-acceptor-substituted molecules is substantially more effective than along cross-conjugation paths in the corresponding geminally substituted derivatives. The nature of the *N*-substituents in $R_2NC_6H_4$-substituted donor-acceptor TEEs was found to strongly influence the position of the intramolecular CT band, with the longest-wavelength absorption being bathochromically shifted in the series R = H, Me, $C_{12}H_{15}$. Also, the two residual $R_3Si-C{\equiv}C$ groups in bis-arylated TEEs make a significant contribution to the overall π-electron delocalization. Protonation of the $R_2NC_6H_4$ group in donor-acceptor TEEs resulted in the complete disappearance of the CT band; upon treatment of the protonated species with base, the initial UV/VIS spectrum was fully regenerated. The presence of a highly polarized electronic excited state in donor-acceptor TEEs was also supported by the strong solvent dependency of their fluorescence spectra. The present investigation, in combination with nonlinear optical, electrochemical, and theoretical studies already in progress, provides a broad view of the structure-function relationships for a large series of unique molecules. Furthermore, the incorporation of selected donor/acceptor-substituted TEEs into oligomers and polymers is currently being pursued. Based on the results already in hand, it can be stated with confidence that donor/acceptor-substituted TEEs represent a promising new class of functional building blocks for the construction of advanced materials.

This work was supported by the *Swiss National Science Foundation*, by a grant from the *ETH Research Council*, and by postdoctoral fellowships from the *U.S. Office of Naval Research* (to *R.R.T.*) and the *Spanish Ministerio de Educación y Ciencia* (to *R.P.C.*). We thank *R. E. Martin*, *B. Hinzen*, *F. Cardullo*, and *U. Neidlein* for high-field NMR measurements and *M. Colussi* for the DSC measurements.

Experimental Part

General. Reagents and solvents were purchased reagent-grade and used without further purification. Compounds **2**, **16**, **25**, **26**, **33**, **56**, and **63** were prepared as described in [6]. Compounds **3** [24], **47** [30], *p*-ethynylaniline [21], *p*-ethynylnitrobenzene [25], *p*-ethynyl-*N*,*N*-dimethylaniline [26], *p*-ethynylanisole [27], and *p*-iodo-*N*,*N*-dimethylaniline [28] were prepared by known methods. Anh. $MgSO_4$ was used as the drying agent after aq. workup. Evaporation and concentration *in vacuo* was done at H_2O-aspirator pressure. All reactions were performed in standard glassware under N_2. A positive pressure of N_2 was essential to the success of [Pd]-catalyzed reactions. Degassing of solvents was accomplished by vigorously bubbling N_2 through the soln. for at least 45 min. Column chromatography (CC): Silica gel-*H* from *Fluka*. TLC: glass or aluminum sheets covered with silica gel *60 F₂₅₄* from *E. Merck*; visualization by UV light or anisaldehyde stain. M.p.: *Büchi SMP-20* apparatus; uncorrected. UV/VIS Spectra: *Varian-Cary-5* spectrophotometer at r.t.; λ_{max} in nm (ε in M^{-1} cm^{-1}). IR Spectra (cm^{-1}): *Perkin-Elmer-1600-FTIR*. ^1H- and ^{13}C-NMR: *Bruker-AMX-500*, *Varian Gemini-200* and *-300* instruments at r.t. in $CDCl_3$ or Cl_2DCCCl_2D; solvent peaks (7.24 and 5.91 ppm for ^1H- and 77.0 and 74.20 ppm for ^{13}C-NMR, resp.) as reference. Fluorescence spectra: *SPEX-1580 Double Spectrophotometer* at r.t. DSC Measurements: *Mettler TA4000 System*. MS (*m/z*): *VG-Tribrid* for EI and *VG-ZAB-2SEQ* instrument for FAB in a 3-nitrobenzyl-alcohol matrix. Elemental analyses were effected by the Mikrolabor in the Laboratorium für Organische Chemie at ETH Zürich.

X-Ray Crystal-Structure Data of **28** ('Structure 2'): $C_{44}H_{62}N_2Si_2$ (M_r = 617.17). Triclinic space group $P\bar{1}$, D_c = 1.024 g cm^{-3}, $Z = 2$, a = 12.684(9), b = 13.059(10), c = 14.512(16) Å, α = 99.48(8), β = 91.86(8), γ = 111.17(6)°, V = 2190(3) Å^3, MoK_α (λ = 0.71073 Å) radiation, $3 \leq 2\theta \leq 40°$, 4090 unique reflections, T = 293 K. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares analysis using experimental weights (heavy atoms anisotropic, H-atoms fixed, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.1068$, $wR(F) = 0.1455$ for 433 variables and 3101 observed reflections with $F > 4\sigma(F)$. Further details of the crystal-structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ (UK) (No. CCDC-10/26).

General Workup for [Pd]-Catalyzed Alkynylations. Unless otherwise noted, [Pd]-catalyzed coupling reactions were worked up as follows. After reacting the aryl or vinyl halide with the terminal alkyne for the designated time period, the solvent Et_3N was removed *in vacuo*. The resulting residue was passed through a plug (SiO_2, CH_2Cl_2), and the solvent was removed to give the crude reaction mixtures which were purified as described in the individual procedures.

N,N-*Didodecyl-4-ethynylaniline* (**5**). Dry K_2CO_3 (20 mg) and **69** (0.525 g, 1.00 mmol) were added to wet THF (5 ml) and MeOH (20 ml), and the mixture was stirred at r.t. for 1 h. Et_2O and H_2O were added, the org. phase was separated, dried, and passed through a plug (SiO_2, CH_2Cl_2) to give **5** (0.451 g, 100%) as an unstable oil. Solns. of **5** were sufficiently stable for use in subsequent reactions without further purification. IR (neat): 3311, 2101, 1609, 1516, 1369. ^1H-NMR (200 MHz, $CDCl_3$): 0.90 (*t*, *J* = 6.6, 6 H); 1.28 (br. *s*, 36 H); 1.57 (*m*, 4 H); 2.96 (*s*, 1 H); 3.26 (*t*, *J* = 7.5, 4 H); 6.53 (*d*, *J* = 8.8, 2 H); 7.33 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 14.30; 22.90; 27.34; 29.56; 29.72; 29.86; 32.14; 51.18; 74.65; 85.40; 107.74; 111.38; 113.72; 148.61.

1-(4-Aminophenyl)-3-[(4-aminophenyl)ethynyl]-6-(triisopropylsilyl)-4-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**6**). A mixture of **3** (0.325 g, 0.595 mmol), *p*-ethynylaniline (0.153 g, 1.31 mmol), $[PdCl_2(PPh_3)_2]$ (40 mg, 0.057 mmol), and CuI (20 mg, 0.11 mmol) in degassed Et_3N (25 ml) was stirred at r.t. for 24 h. Workup and

CC (SiO_2-*H*, CH_2Cl_2/hexane 2:1) gave **6** (0.121 g, 33%). R_f 0.3. Yellow solid. M.p. 165–166°. UV/VIS ($CHCl_3$): 282 (22500), 301 (25300), 428 (45100). IR (CCl_4): 3399, 3361, 3033, 2191, 2181, 2137, 1618, 1516, 1109. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.09 (*s*, 42 H); 3.84 (*s*, 4 H); 6.57 (*d*, *J* = 8.5, 4 H); 7.29 (*d*, *J* = 8.5, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.19; 18.54; 86.06; 99.71; 100.47; 104.62; 112.04; 114.20; 114.52; 118.73; 133.46; 147.32. EI-MS (70 eV): 618 (100, M^+). HR-MS: 618.3818 (M^+, $C_{40}H_{54}N_2Si_2^+$; calc. 618.3825). Anal. calc. for $C_{40}H_{54}N_2Si_2$ (619.06): C 77.61, H 8.79, N 4.53; found: C 77.89, H 8.70, N 4.46.

1-[4-(Dimethylamino)phenyl]-3-{[4-(dimethylamino)phenyl]ethynyl}-6-(triisopropylsilyl)-4-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**7**) *and 3-Bromo-1-[4-(dimethylamino)phenyl]-6-(triisopropylsilyl)-4-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**10**). A mixture of **3** (1.09 g, 2.00 mmol), *p*-ethynyl-*N*,*N*-dimethylaniline (0.290 g, 2.00 mmol), $[PdCl_2(PPh_3)_2]$ (70 mg, 0.10 mmol), and CuI (30 mg, 0.16 mmol) in degassed Et_3N (30 ml) was stirred at r.t. for 24 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 3:1) gave **7** (0.171, 25%) and **10** (0.255 g, 21%).

7: R_f 0.3. Orange solid. M.p. 155–156°. UV/VIS ($CHCl_3$): 300 (31500), 428 (51100). IR (CCl_4): 2200, 2174, 2135, 1607, 1523, 1360, 1110. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.12 (*s*, 42 H); 2.98 (*s*, 12 H); 6.60 (*d*, *J* = 8.8, 4 H); 7.38 (*d*, *J* = 8.8, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.31; 18.67; 40.10; 86.51; 99.86; 100.29; 104.87; 109.47; 111.46; 112.86; 119.06; 133.17; 150.35. EI-MS (70 eV): 674 (100, M^+). Anal. calc. for $C_{44}H_{62}N_2Si_2$ (675.17): C 78.28, H 9.26, N 4.15; found: C 78.10, H 9.38, N 4.23.

10: R_f 0.5. Yellow solid. M.p. 85–86°. UV/VIS ($CHCl_3$): 280 (16600), 318 (17000), 420 (38000). IR (CCl_4): 2180, 2141, 1607, 1535, 1364, 1064. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.10 (*s*, 21 H); 1.10 (*s*, 21 H); 2.99 (*s*, 6 H); 6.59 (*d*, *J* = 9.0, 2 H); 7.32 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.13; 18.50; 39.97; 87.19; 97.53; 101.52; 103.27; 104.09; 105.91; 108.13; 111.49; 111.75; 115.81; 133.32; 150.90. EI-MS (70 eV): 611 (100, M^+). Anal. calc. for $C_{34}H_{52}BrNSi_2$ (610.88): C 66.85, H 8.58, N 2.29; found: C 66.95, H 8.60, N 2.38.

1-[4-(Didodecylamino)phenyl]-3-{[4-(didodecylamino)phenyl]ethynyl}-6-(triisopropylsilyl)-4-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**8**). A mixture of **3** (0.450 g, 0.825 mmol), **5** (0.800 g, 1.77 mmol), $[PdCl_2(PPh_3)_2]$ (30 mg, 0.043 mmol), and CuI (15 mg, 0.079 mmol) in degassed Et_3N (30 ml) was stirred at r.t. for 48 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 20:1) gave **8** (0.470 g, 62%). R_f 0.2. Yellow oil. UV/VIS ($CHCl_3$): 294 (sh, 27400), 312 (30300), 443 (52100). IR (CCl_4): 3092, 2197, 2160, 2133, 1604, 1521. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.87 (*t*, *J* = 6.2, 12 H); 1.10 (*s*, 42 H); 1.25 (br. *s*, 72 H); 1.57 (br. *m*, 8 H); 3.28 (*t*, *J* = 7.4, 8 H); 6.50 (*d*, *J* = 9.0, 4 H); 7.32 (*d*, *J* = 9.0, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.29; 14.02; 18.63; 22.61; 27.06; 27.16; 29.28; 29.44; 29.58; 31.86; 50.89; 86.61; 99.55; 100.68; 105.14; 108.46; 111.03; 112.24; 119.48; 133.47; 148.44. FAB-MS: 1291 (19, M^+), 905 (100). Anal. calc. for $C_{88}H_{150}N_2Si_2$ (1292.36): C 81.79, H 11.70, N 2.17; found: C 81.86, H 11.85, N 2.18.

1-(4-Nitrophenyl)-3-[(4-nitrophenyl)ethynyl]-6-(triisopropylsilyl)-4-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**9**). A mixture of **3** (0.250 g, 0.458 mmol), *p*-ethynylnitrobenzene (0.190 g, 1.30 mmol), $[PdCl_2(PPh_3)_2]$ (35 mg, 0.050 mmol), and CuI (20 mg, 0.11 mmol) in degassed Et_3N (25 ml) was stirred at r.t. for 24 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 2:1) gave **9** (0.147 g, 47%). R_f 0.3. Yellow solid. M.p. 167°. UV/VIS ($CHCl_3$): 314 (29800), 346 (31300), 388 (33200). IR (CCl_4): 2944, 2144, 1594, 1524, 1343. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.08 (*s*, 42 H); 7.63 (*d*, *J* = 9.0, 4 H); 8.19 (*d*, *J* = 9.0, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 11.17; 18.55; 90.83; 96.18; 103.41; 104.83; 115.18; 120.57; 123.54; 129.01; 132.46; 147.45. EI-MS (70 eV): 678 (100, M^+). HR-MS: 678.3334 (M^+, $C_{40}H_{50}N_2O_4Si_2^+$; calc. 678.3309).

1-[4-(Dimethylamino)phenyl]-3-[(4-nitrophenyl)ethynyl]-6-(triisopropylsilyl)-4-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**11**). A mixture of **10** (0.180 g, 0.295 mmol), *p*-ethynylnitrobenzene (0.053 g, 0.36 mmol), $[PdCl_2(PPh_3)_2]$ (10 mg, 0.014 mmol), and CuI (5 mg, 0.03 mmol) in degassed Et_3N (25 ml) was stirred at r.t. for 24 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 4:1) gave **11** (0.050 g, 25%). R_f 0.45. Red solid. M.p. 129–130°. UV/VIS ($CHCl_3$): 295 (27700), 373 (30100), 447 (19900). IR (CCl_4): 3087, 2198, 2172, 2133, 1605, 1520, 1341. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.08 (*s*, 3 H); 1.09 (*s*, 18 H); 1.11 (*s*, 3 H); 1.12 (*s*, 18 H); 2.99 (*s*, 6 H); 6.60 (*d*, *J* = 9.0, 2 H); 7.37 (*d*, *J* = 9.0, 2 H); 7.63 (*d*, *J* = 9.0, 2 H); 8.18 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 11.27; 18.60; 18.65; 40.07; 85.56; 92.32; 94.81; 101.89; 102.13; 102.56; 104.10; 104.20; 108.76; 111.47; 116.42; 117.09; 123.45; 129.67; 132.44; 133.24; 147.19; 150.60. EI-MS (70 eV): 676 (100, M^+). Anal. calc. for $C_{42}H_{56}N_2O_2Si_2$ (677.10): C 74.50, H 8.34, N 4.14; found: C 74.21, H 8.55, N 3.87.

1-(4-Nitrophenyl)-3-[(4-nitrophenyl)ethynyl]-6-phenyl-4-(phenylethynyl)hex-3-ene-1,5-diyne (**12**). A mixture of **4** (0.30 g, 0.71 mmol) and K_2CO_3 (10 mg, 0.07 mmol) in wet THF (2 ml) and MeOH (8 ml) was stirred at r.t. for 2 h. Et_2O and H_2O were added, the org. phase was separated, dried, concentrated to 5 ml, and added to Et_3N (25 ml). The soln. was degassed, *p*-iodonitrobenzene (0.36 g, 1.5 mmol), $[PdCl_2(PPh_3)_2]$ (25 mg, 0.036 mmol), and CuI (10 mg, 0.053 mmol) were added, and the mixture was stirred at r.t. for 18 h. Workup and concentration of the soln. to *ca.* 5 ml resulted in a brown precipitate which was filtered and washed with hexane, then Et_2O to give **12** (262 mg, 71%). Brown solid. M.p. 168° (dec.). UV/VIS ($CHCl_3$): 288 (sh, 30100), 304 (33600), 346 (41200), 426 (36000). IR (CCl_4): 3067, 2178, 1590, 1515, 1340. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.40 (*m*, 6 H); 7.56 (*m*, 4 H); 7.69

(*d*, *J* = 8.9, 4 H); 8.21 (*d*, *J* = 8.9, 4 H). ^{13}C-NMR (50.3 MHz, CDCl$_3$): 87.40; 91.64; 97.03; 101.36; 115.15; 121.36; 122.35; 124.14; 129.03; 129.48; 130.16; 132.19; 132.78; 147.94. FAB-MS: 518 (M^+). Anal. calc. for $C_{34}H_{18}N_2O_4$ (518.13): C 78.76, H 3.50, H 5.40; found: C 78.55, H 3.69, N 5.15.

1-(4-Aminophenyl)-3-[(4-aminophenyl)ethynyl]-6-(4-nitrophenyl)-4-[(4-nitrophenyl)ethynyl]hex-3-ene-1,5-diyne (**13**). A mixture of **6** (0.075 g, 0.12 mmol) and Bu_4NF (0.5 ml, 1M in THF) in wet THF (10 ml) was stirred at r.t. for 0.5 h. Et_2O and H_2O were added, the org. phase was separated, dried, concentrated to *ca.* 1 ml, and added to Et_3N (25 ml). The soln. was degassed, *p*-iodonitrobenzene (0.061 g, 0.25 mmol), [$PdCl_2(PPh_3)_2$] (10 mg, 0.014 mmol), and CuI (5 mg, 0.026 mmol) were added, and the mixture was stirred at r.t. for 24 h. The solvent was removed *in vacuo*, and the residue purified by filtration over a plug (SiO_2, $CHCl_3$) until sparingly soluble **13** was no longer eluted as an orange soln. Evaporation *in vacuo* followed by preparative TLC (SiO_2, CH_2Cl_2) gave **13** (17 mg, 26%). Brown solid. M.p. > 270°. UV/VIS ($CHCl_3$): 304 (27700), 340 (sh, 22300), 420 (27200), 471 (22800). IR (CCl_4): 3383, 3028, 2161, 1605, 1508, 1333. ^{1}H-NMR (200 MHz, (D_8)THF): 5.41 (*s*, 4 H); 6.70 (*d*, *J* = 7.6, 4 H); 7.40 (*d*, *J* = 7.6, 4 H); 7.89 (*d*, *J* = 7.8, 4 H); 8.39 (*d*, *J* = 7.8, 4 H). ^{13}C-NMR (75.5 MHz, (D_8)THF): 88.53; 94.17; 97.51; 106.16; 110.48; 110.99; 115.83; 125.12; 125.78; 131.54; 134.24; 135.48; 149.59; 152.97.

1-[4-(Dimethylamino)phenyl]-3-{[4-(dimethylamino)phenyl]ethynyl}-6-(4-nitrophenyl)-4-[(4-nitrophenyl)ethynyl]hex-3-ene-1,5-diyne (**14**). *Method 1.* A mixture of **7** (0.067 g, 0.10 mmol) and Bu_4NF (0.4 ml, 1M in THF) in wet THF (10 ml) was stirred at r.t. for 0.5 h. Et_2O and H_2O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et_3N (25 ml). The soln. was degassed, *p*-iodonitrobenzene (0.055 g, 0.22 mmol), [$PdCl_2(PPh_3)_2$] (7 mg, 0.01 mmol), and CuI (4 mg, 0.021 mmol) were added, and the mixture was stirred at r.t. for 18 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 1:1) afforded **14** (0.038 g, 63%).

Method 2. A mixture of **21** (0.070 g, 0.11 mmol) and Bu_4NF (0.2 ml, 1M in THF) in wet THF (10 ml) was stirred at r.t. for 0.5 h. Et_2O and H_2O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et_3N (25 ml). The soln. was degassed, *p*-iodonitrobenzene (0.028 g, 0.11 mmol), [$PdCl_2(PPh_3)_2$] (8 mg, 0.011 mmol), and CuI (5 mg, 0.026 mmol) were added, and the mixture stirred at r.t. for 18 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 1:1) gave **14** (0.046 g, 70%). R_f 0.2. Black solid. M.p. 247° (dec.). UV/VIS ($CHCl_3$): 289 (sh, 39500), 315 (45700), 486 (40700). IR (CCl_4): 2164, 1605, 1527, 1330. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.02 (*s*, 12 H); 6.64 (*d*, *J* = 9.0, 4 H); 7.42 (*d*, *J* = 9.0, 4 H); 7.68 (*d*, *J* = 8.9, 4 H); 8.12 (*d*, *J* = 8.9, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 40.04; 87.30; 92.9; 95.8; 103.78; 108.44; 109.6; 111.73; 123.2; 123.80; 130.01; 132.19; 133.42; 147.18; 151.04. FAB-MS: 604 (100, M^+). HR-MS: 604.2108 (M^+, $C_{38}H_{28}N_4O_4^+$; calc. 604.2110).

1-[4-(Didodecylamino)phenyl]-3-{[4-(didodecylamino)phenyl]ethynyl}-6-(4-nitrophenyl)-4-[(4-nitrophenyl)ethynyl]hex-3-ene-1,5-diyne (**15**). A mixture of **8** (0.035 g, 0.027 mmol) and Bu_4NF (0.1 ml, 1M in THF) in wet THF (10 ml) was stirred at r.t. for 0.5 h. Et_2O and H_2O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et_3N (25 ml). The soln. was degassed, *p*-iodonitrobenzene (0.014 g, 0.056 mmol), [$PdCl_2(PPh_3)_2$] (8 mg, 0.011 mmol), and CuI (5 mg, 0.026 mmol) were added, and the mixture was stirred at r.t. for 18 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 5:1) yielded **15** (0.017 g, 52%). R_f 0.1. Black solid. M.p. 64°. UV/VIS ($CHCl_3$): 299 (sh, 45100), 323 (47800), 511 (44600). IR (CCl_4): 3087, 3046, 2164, 1600, 1517, 1339. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86 (*t*, *J* = 6.2, 12 H); 1.25 (br. *s*, 72 H); 1.57 (br. *m*, 8 H); 3.28 (*t*, *J* = 7.4, 8 H); 6.55 (*d*, *J* = 9.0, 4 H); 7.37 (*d*, *J* = 9.0, 4 H); 7.68 (*d*, *J* = 8.9, 4 H); 8.21 (*d*, *J* = 8.9, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 14.12; 22.68; 27.11; 27.22; 29.34; 29.51; 29.65; 31.91; 50.97; 87.42; 93.08; 95.46; 104.16; 107.24; 108.67; 111.20; 123.29; 123.70; 130.05; 132.07; 133.54; 146.98; 148.97. FAB-MS: 1221 (100, M^+). HR-MS: 1220.9032 (M^+, $C_{82}H_{116}N_4O_4^+$; calc. 1220.8996).

1-[4-(Dimethylamino)phenyl]-3-{[4-(dimethylamino)phenyl]ethynyl}-4-[(triisopropylsilyl)ethynyl]-6-(trimethylsilyl)hex-3-ene-1,5-diyne (**17**). A mixture of **16** (1.36 g, 2.95 mmol), *p*-ethynyl-*N*,*N*-dimethylaniline (0.939 g, 6.48 mmol), [$PdCl_2(PPh_3)_2$] (50 mg, 0.071 mmol), and CuI (25 mg, 0.13 mmol) in degassed Et_3N (60 ml) was stirred at r.t. for 40 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 2:1) gave **17** (1.32, g 76%). R_f 0.25. Yellow solid. M.p. 128–129°. UV/VIS ($CHCl_3$): 305 (31600), 430 (52700). IR (CCl_4): 3092, 2199, 2171, 2135, 1606, 1524, 1354, 1108. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.27 (*s*, 9 H); 1.14 (*s*, 21 H); 2.99 (*s*, 12 H); 6.60 (*d*, *J* = 8.9, 2 H); 6.61 (*d*, *J* = 9.0, 2 H); 7.39 (*d*, *J* = 8.9, 2 H); 7.40 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): −0.21; 11.27; 18.57; 39.96; 86.33; 86.81; 100.30; 100.75; 102.74; 102.92; 104.49; 109.28; 111.48; 111.58; 112.62; 120.00; 133.23; 150.56. EI-MS (70 eV): 590 (100, M^+). Anal. calc. for $C_{38}H_{50}N_2Si_2$ (591.00): C 77.23, H 8.53, N 4.74; found: C 77.04, H 8.27, N 4.72.

1-[4-(Didodecylamino)phenyl]-3-{[4-(didodecylamino)phenyl]ethynyl}-4-[(triisopropylsilyl)ethynyl]-6-(trimethylsilyl)hex-3-ene-1,5-diyne (**18**). A mixture of **16** (0.185 g, 0.400 mmol), **5** (0.453 g, 1.00 mmol), [$PdCl_2(PPh_3)_2$] (35 mg, 0.05 mmol), and CuI (15 mg, 0.08 mmol) in degassed Et_3N (20 ml) was stirred at r.t. for 48 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 8:1) gave **18** (0.240 g, 50%). R_f 0.4. Yellow oil. IR (neat): 3088, 3044, 2235, 2200, 2169, 1603, 1367. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.24 (*s*, 9 H); 0.88 (*t*, *J* = 6.5, 12 H); 1.12 (*s*, 21 H); 1.26 (br. *m*, 72 H); 1.54 (*m*, 8 H); 3.24 (*t*, *J* = 7.5, 8 H); 6.51 (*d*, *J* = 8.9, 2 H); 6.53 (*d*, *J* = 8.9, 2 H); 7.32 (*d*, *J* = 8.9, 2 H); 7.34 (*d*, *J* = 8.9, 2 H). ^{13}C-NMR (50.3 MHz, CDCl$_3$): –0.16; 11.35; 14.00; 18.62; 22.60; 27.05; 27.16; 29.27; 29.43; 29.56; 31.85; 50.89; 86.43; 86.86; 99.98; 100.95; 100.99; 102.44; 103.11; 104.71; 108.38; 108.44; 111.06; 111.14; 112.06; 120.25; 133.48; 148.52. FAB-MS (70 eV): 1207 (100, M^+). Anal. calc. for $C_{82}H_{138}N_2Si_2$ (1208.18): C 81.52, H 11.51, N 2.32; found: C 81.32, H 11.60, N 2.24.

1-(4-Methoxyphenyl)-3-[(4-methoxyphenyl)ethynyl]-4-[(triisopropylsilyl)ethynyl]-6-(trimethylsilyl)hex-3-ene-1,5-diyne (**19**). A mixture of **16** (0.600 g, 1.30 mmol), *p*-ethynylanisole (0.365 g, 2.77 mmol), [PdCl$_2$(PPh$_3$)$_2$] (50 mg, 0.071 mmol), and CuI (25 mg, 0.13 mmol) in degassed Et$_3$N (25 ml) was stirred at r.t. for 24 h. Workup and CC (SiO$_2$-*H*, hexane/CH$_2$Cl$_2$ 2:1) gave a yellow oil which crystallized upon standing to give **19** (0.500 g, 68%). R_f 0.4. Yellow solid. M.p. 70–71°. UV/VIS (CHCl$_3$): 277 (23400), 375 (36200), 394 (sh, 34500). IR (CCl$_4$): 2205, 2184, 2139, 1605, 1508, 1251. ^{1}H-NMR (200 MHz, CDCl$_3$): 0.23 (*s*, 9 H); 1.09 (*s*, 21 H); 3.81 (*s*, 6 H); 6.82 (*d*, *J* = 9.0, 2 H); 6.84 (*d*, *J* = 9.0, 2 H); 7.42 (*d*, *J* = 9.0, 2 H); 7.44 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR (50.3 MHz, CDCl$_3$): 0.04; 11.58; 18.89; 55.55; 86.47; 86.94; 99.47; 101.96; 102.62; 104.23; 104.32; 114.29; 114.43; 115.03; 115.08; 115.71; 119.43; 133.83; 160.70; 160.77. EI-MS (70 eV): 564 (45, M^+), 262 (100). Anal. calc. for $C_{36}H_{44}O_2Si_2$ (564.92): C 76.54, H 7.85; found: C 76.27, H 7.91.

1-(4-Nitrophenyl)-3-[(4-nitrophenyl)ethynyl]-4-[(triisopropylsilyl)ethynyl]-6-(trimethylsilyl)hex-3-ene-1,5-diyne (**20**). A mixture of **16** (0.300 g, 0.650 mmol), *p*-ethynylnitrobenzene (0.336 g, 2.28 mmol), [PdCl$_2$(PPh$_3$)$_2$] (80 mg, 0.114 mmol), and CuI (40 mg, 0.21 mmol) in degassed Et$_3$N (30 ml) and THF (40 ml) was stirred at r.t. for 72 h. Workup and CC (SiO$_2$-*H*, hexane/CH$_2$Cl$_2$ 1:1) gave **20** (0.196 g, 51%). R_f 0.3. Yellow solid. M.p. 150–151° (dec.). UV/VIS (CHCl$_3$): 329 (29900), 346 (33700), 387 (sh, 33400). IR (CCl$_4$): 3081, 2944, 2144, 1592, 1343, 1251. ^{1}H-NMR (300 MHz, CDCl$_3$): 0.24 (*s*, 9 H); 1.09 (*s*, 21 H); 7.63 (*d*, *J* = 9.0, 2 H); 7.65 (*d*, *J* = 9.0, 2 H); 8.20 (*d*, *J* = 9.0, 2 H); 8.22 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR (75.5 MHz, CDCl$_3$): –0.36; 11.21; 18.56; 90.59; 90.99; 96.37; 96.45; 101.23; 102.96; 105.28; 107.30; 115.98; 120.46; 123.53; 123.65; 128.93; 128.99; 132.44; 132.47; 147.46. EI-MS (70 eV): 594 (26, M^+), 551 (34, $[M - (\text{i-Pr})]^+$), 73 (100, $[Me_3Si]^+$). Anal. calc. for $C_{34}H_{38}N_2O_4Si_2$ (594.86): C 68.65, H 6.44, N 4.71; found: C 68.79, H 6.58, N 4.66.

1-[4-(Dimethylamino)phenyl]-3-{[4-(dimethylamino)phenyl]ethynyl}-4-[(4-nitrophenyl)ethynyl]-6-(triisopropylsilyl)hex-3-ene-1,5-diyne (**21**). A mixture of **17** (0.300 g, 0.508 mmol) and K$_2$CO$_3$ (10 mg, 0.07 mmol) in wet THF (5 ml) and MeOH (20 ml) was stirred at r.t. for 2 h. Et$_2$O and H$_2$O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et$_3$N (40 ml). The soln. was degassed, *p*-iodonitrobenzene (0.126 g, 0.506 mmol), [PdCl$_2$(PPh$_3$)$_2$] (20 mg, 0.029 mmol), and CuI (8 mg, 0.042 mmol) were added, and the mixture was stirred at r.t. for 18 h. Workup and CC (SiO$_2$-*H*, hexane/Et$_2$O 1:1) provided **21** (255 mg, 79%). R_f 0.2. Red solid. M.p. 169–170° (dec.). UV/VIS (CHCl$_3$): 304 (40500), 364 (18900), 461 (38200). IR (CCl$_4$): 3089, 2208, 2161, 2133, 1605, 1521, 1336. ^{1}H-NMR (200 MHz, Cl$_2$DCCDCl$_2$): 1.14 (*s*, 21 H); 3.00 (2*s*, 12 H); 6.61 (*d*, *J* = 9.0, 2 H); 6.63 (*d*, *J* = 9.0, 2 H); 7.39 (*d*, *J* = 9.0, 2 H); 7.40 (*d*, *J* = 9.0, 2 H); 7.61 (*d*, *J* = 9.0, 2 H); 8.18 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR (50.3 MHz, CDCl$_3$): 11.26; 18.63; 39.99; 86.81; 87.03; 94.17; 94.87; 101.03; 101.98; 103.63; 108.90; 109.03; 111.31; 111.54; 111.73; 121.34; 123.69; 130.36; 132.14; 133.18; 133.47; 146.99; 150.74; 150.80. EI-MS (70 eV): 639 (100, M^+). HR-MS: 639.3285 (M^+, $C_{41}H_{45}N_3O_2Si^+$, calc. 639.3281).

1-(4-Methoxyphenyl)-3-[(4-methoxyphenyl)ethynyl]-4-[(4-nitrophenyl)ethynyl]-6-(triisopropylsilyl)hex-3-ene-1,5-diyne (**22**). A mixture of **19** (0.510 g, 0.904 mmol) and K$_2$CO$_3$ (10 mg, 0.07 mmol) in wet THF (5 ml) and MeOH (15 ml) was stirred at r.t. for 2 h. Et$_2$O and H$_2$O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et$_3$N (20 ml). The soln. was degassed, *p*-iodonitrobenzene (0.224 g, 0.900 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 at r.t. for 24 h. Workup and CC (SiO$_2$-*H*, hexane/Et$_2$O 1:1) afforded **22** (0.350 g, 63%). R_f 0.4. Yellow solid. M.p. 131–133° (dec.). UV/VIS (CHCl$_3$): 295 (30200), 385 (27900), 428 (28900). IR (CCl$_4$): 3077, 3005, 2212, 2179, 2133, 1604, 1511, 1341, 1251. ^{1}H-NMR (200 MHz, CDCl$_3$): 1.16 (*s*, 21 H); 3.84 (*s*, 6 H); 6.90 (*d*, *J* = 8.8, 4 H); 7.49 (*d*, *J* = 8.8, 4 H); 7.64 (*d*, *J* = 8.6, 2 H); 8.22 (*d*, *J* = 8.6, 2 H). ^{13}C-NMR (50.3 MHz, CDCl$_3$): 11.19; 18.66; 55.27; 86.34; 86.59; 93.03; 95.39; 100.14; 100.20; 102.39; 103.00; 114.00; 114.27; 114.38; 120.20; 123.71; 129.78; 132.27; 133.38; 133.61; 147.25; 160.61; 160.65. EI-MS (70 eV): 613 (11, M^+), 183 (100). HR-MS: 613.2650 (M^+, $C_{39}H_{39}NO_4Si^+$; calc. 613.2648).

1-(4-Nitrophenyl)-3,4-bis[(4-nitrophenyl)ethynyl]-6-(triisopropylsilyl)hex-3-ene-1,5-diyne (**23**). A mixture of **20** (0.060 g, 0.101 mmol) and K$_2$CO$_3$ (10 mg, 0.07 mmol) in THF (2 ml) and MeOH (10 ml) was stirred at r.t. for 0.5 h. Et$_2$O and H$_2$O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et$_3$N (25 ml). The soln. was degassed, *p*-iodonitrobenzene (0.050 g, 0.200 mmol), [PdCl$_2$(PPh$_3$)$_2$] (25 mg, 0.036 mmol), and CuI (15 mg, 0.079 mmol) were added, and the mixture was stirred at r.t. for 24 h. Workup and CC (SiO$_2$-*H*, hexane/CH$_2$Cl$_2$ 1:1) gave **23** (0.012 g, 18%). R_f 0.2. Yellow solid. M.p. 182–183° (dec.). UV (CHCl$_3$): 326 (42100), 344 (37300), 403 (35100). IR (CCl$_4$): 3111, 3078, 2189, 1594, 1517, 1339. ^{1}H-NMR (200 MHz, CDCl$_3$): 1.10 (*s*, 3 H); 1.11 (*s*, 18 H); 7.63 (*m*, 4 H); 7.67 (*d*, *J* = 8.2, 2 H); 8.23 (*m*, 6 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.12; 18.54; 90.61; 90.73; 91.51; 97.16; 97.33; 102.32; 106.26; 117.00; 119.31; 123.70; 123.94; 128.78; 132.55; 132.67; 147.79; 147.86. EI-MS (70 eV): 643 (4, M^+), 600 (6, $[M-(\text{i-Pr})]^+$), 44 (100). HR-MS: 643.2078 (M^+, $C_{37}H_{33}N_3O_6Si^+$; calc. 643.2138).

1-[4-(Dimethylamino)phenyl]-3,4-bis{[4-(dimethylamino)phenyl]ethynyl}-6-(triisopropylsilyl)hex-3-ene-1,5-diyne (**24**). A mixture of **17** (0.400 g, 0.678 mmol) and K_2CO_3 (10 mg, 0.07 mmol) in wet THF (5 ml) and MeOH (20 ml) was stirred at r.t. for 2 h. Et_2O and H_2O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et_3N (50 ml). The soln. was degassed, *p*-iodo-*N,N*-dimethylaniline (0.167 g, 0.676 mmol), $[PdCl_2(PPh_3)_2]$ (25 mg, 0.036 mmol), and CuI (10 mg, 0.053 mmol) were added, and the mixture was stirred at r.t. for 24 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 1:1) gave **24** (81 mg, 19%). R_f 0.5. Dark-yellow solid. M.p. 165–166°. UV/VIS ($CHCl_3$): 281 (sh, 35800), 305 (41800), 431 (44600), 471 (44300). IR (CCl_4): 3092, 3041, 2199, 2173, 2122, 1604, 1521, 1366, 1196. ^{1}H-NMR (300 MHz, $Cl_2DCCDCl_2$): 1.08 (*s*, 21 H); 2.93 (*s*, 18 H); 6.57 (*m*, 6 H); 7.33 (*m*, 4 H); 7.37 (*d*, *J* = 8.7, 2 H). ^{13}C-NMR (75.5 MHz, $Cl_2DCCDCl_2$): 11.68; 19.10; 40.45; 87.10; 87.37; 87.90; 100.07; 100.11; 100.28; 100.57; 104.84; 109.51; 109.65; 111.88; 112.03; 112.07; 113.92; 116.74; 133.20; 133.35; 133.39; 150.59; 150.66. EI-MS (70 eV): 637 (100, M^+). HR-MS: 637.3855 (M^+, $C_{43}H_{51}N_3Si^+$; calc. 637.3852).

*4-Iodo-*N,N*-didodecylaniline* (**27**). To a soln. of *p*-iodoaniline (11.56 g, 52.78 mmol) in DMF (160 ml) was added 1-iodododecane (42.9 ml, 174 mmol) and Na_2CO_3 (9.6 g, 91 mmol), and the mixture was stirred at 120° for 20 h. The solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2, and passed through a plug of *Celite*. CC (SiO_2, hexane/CH_2Cl_2 10:1) gave **27** (10.5 g, 36%). R_f 0.6. Clear oil. IR (CCl_4): 2922, 1589, 1369, 1194, 1116. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.89 (*t*, *J* = 6.5, 6 H); 1.29 (*m*, 36 H); 1.56 (*m*, 4 H); 3.22 (*t*, *J* = 7.5, 4 H); 6.41 (*d*, *J* = 8.7, 2 H); 7.42 (*d*, *J* = 8.7, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 13.9; 22.4; 26.8; 26.9; 29.0; 29.1; 29.3; 29.4; 31.7; 50.7; 75.0; 113.7; 137.3; 147.3. FAB-MS: 554 (100, M^+). Anal. calc. for $C_{30}H_{54}NI$ (555.68): C 64.85, H 9.79, H 2.52; found: C 64.92, H 9.73, N 2.36.

*(*E*)-1,6-Bis[4-(dimethylamino)phenyl]-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**28**). A mixture of **26** (0.325 g, 0.745 mmol), *p*-iodo-*N,N*-dimethylaniline (0.368 g, 1.49 mmol), $[PdCl_2(PPh_3)_2]$ (30 mg, 0.043 mmol), and CuI (15 mg, 0.079 mmol) in degassed Et_3N (30 ml) was stirred at r.t. for 24 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 2:1) afforded **28** (0.216 g, 43%) besides dimeric **52** (20 mg, 5%). R_f 0.4. Yellow solid. M.p. 217–218°. UV/VIS ($CHCl_3$): 292 (37700), 459 (41000). IR (KBr): 2196, 2136, 1604, 1527, 1366. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.13 (*s*, 42 H); 3.00 (*s*, 12 H); 6.62 (*d*, *J* = 9.0, 4 H); 7.34 (*d*, *J* = 9.0, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.09; 18.46; 39.89; 86.80; 99.80; 100.10; 104.20; 109.52; 111.29; 114.80; 132.75; 150.02. EI-MS (70 eV): 674 (11, M^+), 91 (100). Anal. calc. for $C_{44}H_{62}N_2Si_2$ (675.17): C 78.28, H 9.26, N 4.15; found: C 78.01, H 9.01, N 4.29. X-Ray: *Fig. 8*.

*(*E*)-1,6-Bis[4-(didodecylamino)phenyl]-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**29**). A mixture of **26** (0.200 g, 0.459 mmol), **27** (0.460 g, 0.829 mmol), $[PdCl_2(PPh_3)_2]$ (20 mg, 0.029 mmol), and CuI (10 mg, 0.053 mmol) in degassed Et_3N (20 ml) was stirred at r.t. for 24 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 7:1) yielded **29** (0.150 g, 28%). R_f 0.5. Yellow oil. UV/VIS ($CHCl_3$): 299 (43900), 478 (55200). IR (CCl_4): 3092, 3041, 2194, 2139, 1603, 1518 1364. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.90 (*t*, *J* = 6.3, 12 H); 0.14 (*s*, 42 H); 1.21 (br. *s*, 72 H); 1.55 (br. *m*, 8 H); 3.28 (*t*, *J* = 7.5, 8 H); 6.54 (*d*, *J* = 8.9, 4 H); 7.30 (*d*, *J* = 8.9, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.59; 14.30; 18.94; 22.90; 27.35; 27.46; 29.57; 29.73; 29.87; 32.15; 51.20; 87.27; 100.25; 100.49; 105.02; 108.98; 111.38; 116.05; 133.56; 148.61. FAB-MS: 1291 (M^+). Anal. calc. for $C_{88}H_{150}N_2Si_2$ (1292.36): C 81.79, H 11.70, N 2.17; found: C 81.70, H 11.57, N 2.13.

*(*E*)-1,6-Bis(4-nitrophenyl)-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**30**). A mixture of **26** (0.100 g, 0.229 mmol), *p*-iodonitrobenzene (0.115 g, 0.462 mmol), $[PdCl_2(PPh_3)_2]$ (40 mg, 0.057 mmol), and CuI (20 mg, 0.11 mmol) in degassed Et_3N (30 ml) was stirred at r.t. for 24 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 3:1) gave **30** (0.140 g, 90%). R_f 0.3. Yellow solid. M.p. 225–226° (dec.). UV/VIS ($CHCl_3$): 310 (37600), 403 (34000). IR (CCl_4): 3095, 2195, 2136, 1604, 1522, 1359. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.08 (*s*, 6 H); 1.09 (*s*, 36 H); 7.60 (*d*, *J* = 9.0, 4 H); 8.20 (*d*, *J* = 9.0, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.22; 18.62; 91.73; 96.26; 102.51; 104.55; 117.96; 123.56; 129.11; 132.49; 147.47. EI-MS (70 eV): 678 (100, M^+). Anal. calc. for $C_{40}H_{50}N_2O_4Si_2$ (679.03): C 70.75, H 7.42, N 4.13; found: C 70.75, H 7.26, N 4.20. X-Ray: *Fig. 9*.

*(*E*)-1,6-Bis[4-(dimethylamino)phenyl]-3,4-bis[(4-nitrophenyl)ethynyl]hex-3-ene-1,5-diyne* (**31**). A soln. of **28** (36 mg, 0.053 mmol) and Bu_4NF (0.2 ml, 1M in THF) in wet THF (10 ml) was stirred at r.t. for 0.5 h. Et_2O and H_2O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et_3N (10 ml) and THF (10 ml). The soln. was degassed, *p*-iodonitrobenzene (0.029 g, 0.12 mmol), $[PdCl_2(PPh_3)_2]$ (4 mg, 0.006 mmol), and CuI (2 mg, 0.01 mmol) were added, and the mixture was stirred at r.t. for 12 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 1:1) gave **31** (18 mg, 56%). R_f 0.4. Black solid. M.p. 255° (dec.). UV/VIS ($CHCl_3$): 300 (37900), 393 (48300), 533 (22000). IR (CCl_4): 3072, 3039, 2161, 1601, 1526, 1331. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.05 (*s*, 12 H);

6.66 (*d*, *J* = 8.9, 4 H); 7.42 (*d*, *J* = 8.9, 4 H); 7.73 (*d*, *J* = 8.8, 4 H); 8.24 (*d*, *J* = 8.8, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 40.1; 86.3; 93.0; 96.0; 102.8; 108.6; 111.7; 116.2; 123.7; 129.8; 132.4; 133.1; 147.3; 150.8. FAB-MS: 604 (6, M^+), 69 (100). HR-MS: 604.2121 (M^+, $C_{38}H_{28}N_4O_4^+$; calc. 604.2110).

(E)-1,6-Bis[4-(didodecylamino)phenyl]-3,4-bis[(4-nitrophenyl)ethynyl]hex-3-ene-1,5-diyne (**32**). A soln. of **29** (0.075 g 0.058 mmol) and Bu_4NF (0.3 ml, 1M in THF) in wet THF (10 ml) was stirred at r.t. for 0.5 h. Et_2O and H_2O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et_3N (25 ml). The soln. was degassed, *p*-iodonitrobenzene (0.035 g, 0.14 mmol), $[PdCl_2(PPh_3)_2]$ (25 mg, 0.036 mmol) and CuI (10 mg, 0.053 mmol) were added, and the mixture stirred at r.t. for 4 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 5:1) gave **32** (0.024 g, 34%). R_f 0.1. Black solid. M.p. 84°. UV/VIS ($CHCl_3$): 303 (48200), 399 (55300), 556 (24700). IR (CCl_4): 2921, 2211, 2169, 1602, 1520, 1338. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86 (*m*, 12 H); 1.25 (br. *m*, 72 H); 1.57 (*m*, 8 H); 3.28 (*t*, *J* = 7.6, 8 H); 6.55 (*d*, *J* = 9.0, 4 H); 7.34 (*d*, *J* = 9.0, 4 H); 7.70 (*d*, *J* = 9.0, 4 H); 8.21 (*d*, *J* = 9.0, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 14.12; 22.69; 27.13; 27.24; 29.35; 29.52; 29.66; 31.92; 50.97; 86.30; 93.13; 95.77; 102.90; 107.44; 111.22; 115.99; 123.69; 129.84; 132.39; 133.20; 147.21; 148.77. FAB-MS: 1221 (100, M^+). HR-MS: 1220.9001 (M^+, $C_{82}H_{116}N_4O_4^+$; calc. 1220.8996). Anal. calc. for $C_{82}H_{116}N_4O_4$ (1221.86): C 80.61, H 9.57, N 4.59; found: C 80.57, H 9.65, N 4.73.

(E)-1,6-Bis(4-nitrophenyl)-3,4-bis(phenylethynyl)hex-3-ene-1,5-diyne (**34**). A soln. of **33** (0.13 g, 0.31 mmol) and K_2CO_3 (25 mg, 0.18 mmol) in wet THF (2 ml) and MeOH (8 ml) was stirred at r.t. for 2 h. Et_2O and H_2O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et_3N (25 ml). The soln. was degassed, *p*-iodonitrobenzene (0.170 g, 0.68 mmol), $[PdCl_2(PPh_3)_2]$ (20 mg, 0.029 mmol), and CuI (10 mg, 0.053 mmol) were added, and the mixture was stirred at r.t. for 18 h. Workup and concentration of the soln. to *ca.* 5 ml afforded a red precipitate which was filtered, washed with hexane and Et_2O to give **34** (31 mg, 19%). Red solid. M.p. 205–210° (dec.). UV/VIS ($CHCl_3$): 338 (45800), 427 (29900). IR (CCl_4): 3108, 3078, 2187, 2177, 1591, 1516, 1346. ^{1}H-NMR (300 MHz, $Cl_2DCCDCl_2$): 7.34 (*m*, 6 H); 7.51 (*m*, 4 H); 7.65 (*d*, *J* = 7.3, 4 H); 8.15 (*d*, *J* = 7.3, 4 H). ^{13}C-NMR (75.5 MHz, $Cl_2DCCDCl_2$): 86.99; 92.11; 97.43; 100.92; 118.12; 122.17; 124.08; 129.04; 129.38; 130.13; 132.08; 132.02; 147.70. EI-MS (70 eV): 518 (100, M^+). HR-MS: 518.1296 (M^+, $C_{34}H_{18}N_2O_4^+$; calc. 518.1266).

(Z)-1,6-Bis[4-(dimethylamino)phenyl]-3,4-bis[(4-nitrophenyl)ethynyl]hex-3-ene-1,5-diyne (**35**). A soln. of **31** (15 mg, 0.025 mmol) in $CHCl_3$ (75 ml) was irradiated (366 nm) in a quartz flask for 6 h at r.t. Removal of the solvent and repeated CC (SiO_2-*H*, hexane/CH_2Cl_2 1:1) gave **35** (3 mg, 20%) and recovered **31** (10 mg). R_f 0.38 (**31**: R_f 0.40). Black solid. M.p. 211 (dec.). UV/VIS ($CHCl_3$): 305 (40500), 389 (24200), 448 (30100), 520 (23800). IR (CCl_4): 2167, 1606, 1522, 1328. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.02 (*s*, 12 H); 6.64 (*d*, *J* = 9.1, 4 H); 7.45 (*d*, *J* = 9.1, 4 H); 7.65 (*d*, *J* = 9.1, 4 H); 8.20 (*d*, *J* = 9.1, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 40.03; 86.64; 92.79; 95.81; 103.21; 108.84; 111.77; 116.04; 123.85; 129.74; 132.33; 133.64; 147.42; 150.90. FAB-MS: 604 (100, M^+). HR-MS: 604.2095 (M^+, $C_{38}H_{28}N_4O_4^+$; calc. 604.2110).

(Z)-1,1-Dibromo-3,4-bis[(triisopropylsilyl)ethynyl]-6-(trimethylsilyl)hexa-1,3-diene-5-yne (**36**). To a soln. of **25** (2.00 g, 2.65 mmol) in THF (800 ml) at −78° was slowly added 0.3M LDA in THF (30.0 ml, 10.0 mmol; prepared by the addition of 1.6M BuLi in hexane (6.25 ml, 10.0 mmol) to a soln. of $(i\text{-}Pr)_2NH$ (1.4 ml, 7.8 mmol) in dry THF (22 ml) at 0°). The green mixture was stirred for 30 min and then slowly warmed to −20°. Me_3SiCl (1.3 ml, 10.3 mmol) was added, and the resulting soln. stirred at r.t. for 1 h. Sat. aq. NH_4Cl soln. (20 ml) was added, and the mixture was then poured into hexane (400 ml). Extraction with H_2O (4 × 150 ml) and sat. aq. NaCl soln. (200 ml), drying, evaporation *in vacuo*, and CC (SiO_2, hexane) afforded **36** (1.39 g, 80%). R_f 0.6. Clear solid. M.p. 63°. IR (CCl_4): 3302, 2942, 2179, 2146, 2101, 1576, 1220, 1195, 1071. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.20 (*s*, 9 H); 1.09 (*s*, 6 H); 1.11 (*s*, 18 H); 1.12 (*s*, 18 H); 7.64 (*s*, 1 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): −0.2; 11.5; 18.8; 94.9; 101.1; 102.5; 103.1; 104.8; 105.5; 109.2; 115.8; 131.4; 133.6. EI-MS (70 eV): 668 (4, M^+), 73 (100, $[Me_3Si]^+$). Anal. calc. for $C_{31}H_{52}Br_2Si_3$ (668.82): C 55.67, H 7.84; found: C 55.93, H 7.84.

(E)-3,4-Bis[(triisopropylsilyl)ethynyl]-1-(trimethylsilyl)hex-3-ene-1,5-diyne (**37**). To a soln. of **36** (1.40 g, 2.09 mmol) in dry THF (150 ml) at −78° was added slowly 0.3M LDA in THF (24.5 ml, 7.35 mmol; prepared by the addition of 1.6M BuLi in hexane (4.9 ml, 7.8 mmol) to a soln. of $(i\text{-}Pr)_2NH$ (1.1 ml, 7.8 mmol) in dry THF (20 ml) at 0°). After warming to −20° within 1 h, sat. aq. NH_4Cl soln. (20 ml) was added. The mixture was diluted with hexane (300 ml), extracted with H_2O (4 × 150 ml), then with sat. aq. NaCl soln. (150 ml), dried, and the solvent was removed *in vacuo*. CC (SiO_2, hexane) yielded **37** (0.97 g, 91%). R_f 0.5. Pale yellow oil. IR (neat): 3307, 2944, 2135, 2122, 2080, 1251, 1186, 1017. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.20 (*s*, 9 H); 1.10 (*s*, 6 H); 1.11 (*s*, 36 H); 3.46 (*s*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): −0.3; 11.4; 18.8; 81.0; 86.1; 101.4; 102.9; 103.1; 103.2; 103.5; 105.6; 117.3; 120.0. EI-MS: 508 (23, M^+), 465 (6, $[M - (i\text{-}Pr)]^+$), 73 (100, $[Me_3Si]^+$). HR-MS: 508.3341 (M^+, $C_{31}H_{52}Si_3^+$; calc. 508.3377).

(E)-1-[4-(Dimethylamino)phenyl]-3,4-bis[(triisopropylsilyl)ethynyl]-6-(trimethylsilyl)hex-3-ene-1,5-diyne (**38**). A mixture of **37** (0.350 g, 0.690 mmol), *p*-iodo-*N*,*N*-dimethylaniline (0.186 g, 0.753 mmol), $[PdCl_2(PPh_3)_2]$

(44 mg, 0.063 mmol), and CuI (22 mg, 0.12 mmol) in degassed Et_3N (50 ml) was stirred at r.t. for 24 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 2:1) gave **38** (0.212 g, 50%). R_f 0.7. Yellow-brown solid. M.p. 115–116°. UV/VIS ($CHCl_3$): 289 (24000), 335 (18900), 433 (29300). IR (CCl_4): 3087, 2190, 2133, 1605. ^1H-NMR (200 MHz, $CDCl_3$): 0.20 (*s*, 9 H); 1.11 (*s*, 21 H); 1.12 (*s*, 21 H); 2.98 (*s*, 6 H); 6.58 (*d*, *J* = 8.6, 2 H); 7.32 (*d*, *J* = 8.6, 2 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): −0.28; 11.26; 11.36; 18.67; 18.74; 40.09; 86.69; 101.11; 101.23; 101.27; 102.28; 103.49; 103.77; 104.20; 109.26; 111.51; 114.76; 118.74; 133.17; 150.48. EI-MS: (70 eV): 628 (100, M^+). Anal. calc. for $C_{39}H_{61}NSi_3$ (628.18): C 74.57, H 9.79, N 2.23; found: C 74.37, H 9.65, N 2.36.

*(*E*)-1-[4-(Didodecylamino)phenyl]-3,4-bis[(triisopropylsilyl)ethynyl]-6-(trimethylsilyl)hex-3-ene-1,5-diyne* (**39**). A mixture of **37** (0.610 g, 1.20 mmol), **27** (0.727 g, 1.31 mmol), $[PdCl_2(PPh_3)_2]$ (77 mg, 0.11 mmol), and CuI (38 mg, 0.20 mmol) in degassed Et_3N (40 ml) was stirred at r.t. for 16 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 4:1) gave **39** (0.179 g, 16%). R_f 0.5. Orange oil. UV/VIS ($CHCl_3$): 274 (20500), 290 (23850), 300 (24200), 327 (sh, 19400), 336 (19900), 350 (17000), 448 (32100). IR (film): 2922, 2188, 2133, 1606, 1522, 1180. ^1H-NMR (500 MHz, $CDCl_3$): 0.20 (*s*, 9 H); 0.89 (*t*, *J* = 6.4, 6 H); 1.12 (*s*, 3 H); 1.13 (*s*, 3 H); 1.14 (*s*, 18 H); 1.15 (*s*, 18 H); 1.27 (*m*, 36 H); 1.55 (*m*, 4 H); 3.27 (*t*, *J* = 7.5, 4 H); 6.52 (*d*, *J* = 8.6, 2 H); 7.29 (*d*, *J* = 8.6, 2 H). ^{13}C-NMR (125.7 MHz, $CDCl_3$): −0.3; 11.2; 11.3; 14.1; 18.6; 18.7; 22.7; 27.1; 27.2; 29.3; 29.5; 29.6; 29.7; 31.6; 31.9; 35.0; 50.9; 86.7; 100.9; 101.1; 101.7; 102.4; 103.3; 103.9; 104.2; 108.1; 111.0; 114.3; 118.9; 133.4; 148.4. FAB-MS: 936 (M^+). Anal. calc. for $C_{61}H_{105}NSi_3$ (936.78): C 78.21, H 11.30, N 1.50; found: C 78.27, H 11.30, N 1.77.

*(*E*)-1-(4-Nitrophenyl)-3,4-bis[(triisopropylsilyl)ethynyl]-6-(trimethylsilyl)hex-3-ene-1,5-diyne* (**40**). A soln. of **37** (0.382 g, 0.752 mmol), *p*-iodonitrobenzene (0.206 g, 0.827 mmol), $[PdCl_2(PPh_3)_2]$ (48 mg, 0.068 mmol), and CuI (24 mg, 0.13 mmol) in degassed Et_3N (50 ml) was stirred at r.t. for 24 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 2:1) afforded **40** (0.375 g, 80%). R_f 0.6. Yellow solid. M.p. 120–121°. UV/VIS ($CHCl_3$): 311 (27300), 358 (22800), 382 (26500). IR (CCl_4): 2148, 1594, 1523, 1343. ^1H-NMR (200 MHz, $CDCl_3$): 0.21 (*s*, 9 H); 1.09 (*s*, 21 H); 1.13 (*s*, 21 H); 7.59 (*d*, *J* = 8.8, 2 H); 8.19 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): −0.44; 11.24; 18.58; 18.69; 91.99; 95.43; 101.42; 102.42; 103.24; 103.49; 103.55; 106.19; 116.59; 119.14; 123.49; 129.43; 147.40; 147.28. EI-MS (70 eV): 629 (14, M^+), 73 (100, $[Me_3Si]^+$). Anal. calc. for $C_{37}H_{55}NO_2Si_3$ (630.11): C 70.53, H 8.80, N 2.22; found: C 70.53, H 8.64, N 2.23.

*(*E*)-1-[4-(Dimethylamino)phenyl]-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**41**). A mixture of **38** (0.100 g, 0.159 mmol) and K_2CO_3 (10 mg, 0.07 mmol) in wet THF (1 ml) and MeOH (5 ml) was stirred at r.t. for 0.5 h. Et_2O and H_2O were added, the org. phase was separated, dried, and removal of the solvent *in vacuo* gave **41** (0.087 g, 99%) as a relatively unstable yellow solid. R_f (SiO_2, hexane/CH_2Cl_2 2:1) 0.3. IR (CCl_4): 3301, 2184, 2141, 2092, 1606. ^1H-NMR (200 MHz, $CDCl_3$): 1.13 (*s*, 42 H); 3.00 (*s*, 6 H); 3.44 (*s*, 1 H); 6.61 (*d*, *J* = 8.9, 2 H); 7.34 (*d*, *J* = 8.9, 2 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.05; 18.40; 39.82; 81.08; 84.57; 85.97; 101.18; 101.31; 101.56; 103.25; 108.79; 111.23; 111.33; 113.61; 120.35; 132.95; 150.28. EI-MS (70 eV): 555 (100, M^+), 512 (4, $[M - (i\text{-}Pr)]^+$).

*(*E*)-1-[(4-Nitrophenyl)ethynyl]-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**43**). A mixture of **40** (0.100 g, 0.159 mmol) and K_2CO_3 (10 mg, 0.07 mmol) in wet THF (1 ml) and MeOH (5 ml) was stirred at r.t. for 0.5 h. Et_2O and H_2O were added, the org. phase was separated, dried, and removal of the solvent *in vacuo* gave **43** (0.084 g, 95%) as a relatively unstable yellow solid. IR (CCl_4): 3258, 2149, 2094, 1594, 1522, 1342. ^1H-NMR (300 MHz, $CDCl_3$): 1.08 (*s*, 3 H); 1.09 (*s*, 18 H); 1.12 (*s*, 3 H); 1.13 (*s*, 18 H); 3.55 (*s*, 1 H); 7.61 (*d*, *J* = 9.0, 2 H); 8.21 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.2; 18.6; 81.0; 86.8; 91.7; 95.9; 102.1; 102.9; 103.9; 104.2; 118.4; 119.0; 123.5; 129.8; 132.5; 147.8. EI-MS (70 eV): 557 (29, M^+), 514 (79, $[M - (i\text{-}Pr)]^+$), 41 (100).

*(*E*)-1-[4-(Dimethylamino)phenyl]-6-(4-nitrophenyl)-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**44**). A mixture of **38** (0.230 g, 0.367 mmol) and 10 mg of dry K_2CO_3 in wet THF (5 ml) and MeOH (15 ml) was stirred at r.t. for 2 h. Et_2O and H_2O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et_3N (35 ml). The soln. was degassed, *p*-iodonitrobenzene (0.094 g, 0.38 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 at r.t. for 24 h. Workup and CC (SiO_2-*H*, hexane/Et_2O 10:1) provided **44** (0.163 g, 66%). R_f 0.3. Dark-red solid. M.p. 190–191° (dec.). UV/VIS ($CHCl_3$): 294 (37000), 352 (16300), 468 (31200). IR (CCl_4): 3094, 2182, 2165, 2144, 1600, 1519, 1337. ^1H-NMR (500 MHz, $CDCl_3$): 1.13 (*s*, 3 H); 1.14 (*s*, 18 H); 1.16 (*s*, 3 H); 1.17 (*s*, 18 H); 3.30 (*s*, 6 H); 6.64 (*d*, *J* = 8.9, 2 H); 7.37 (*d*, *J* = 8.9, 2 H); 7.61 (*d*, *J* = 8.6, 2 H); 8.21 (*d*, *J* = 8.6, 2 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 11.28; 11.32; 18.64; 18.69; 40.06; 87.13; 93.06; 94.70; 102.14; 102.33; 102.70; 103.23; 103.85; 108.87; 111.53; 113.34; 120.18; 123.48; 129.91; 132.26; 133.09; 147.08; 150.69. EI-MS (70 eV): 676 (M^+). Anal. calc. for $C_{42}H_{56}N_2O_2Si_2$ (677.10): C 74.50, H 8.34, N 4.14; found: C 74.23, H 8.23, N 4.22. X-ray [13].

*(*E*)-1-[4-(Didodecylamino)phenyl]-6-(4-nitrophenyl)-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**45**). A mixture of **39** (0.120 g, 0.128 mmol) and K_2CO_3 (30 mg, 0.22 mmol) in wet THF (1 ml) and MeOH (5 ml) was stirred at r.t. for 2 h. Et_2O and H_2O were added, the org. phase was separated and dried, the solvent was

removed *in vacuo*, and the residue filtered through a short column ($\mathrm{SiO_2}$, hexane/$\mathrm{CH_2Cl_2}$ 1:1). The product fractions were reduced to 5 ml, and this soln. was added to $\mathrm{Et_3N}$ (35 ml). After degassing, *p*-iodonitrobenzene (0.032 g, 0.128 mmol), $[\mathrm{PdCl_2(PPh_3)_2}]$ (10 mg, 0.014 mmol), and CuI (5 mg, 0.026 mmol) were added, and the mixture was stirred at r.t. for 16 h. Workup and CC ($\mathrm{SiO_2}$-*H*, hexane/$\mathrm{CH_2Cl_2}$ 6:1) gave **45** (0.060 g, 48%). R_f 0.5. Red oil. UV/VIS ($\mathrm{CHCl_3}$): 297 (30500), 357 (13120), 488 (25700). IR (film): 2922, 2180, 2167, 2152, 1604, 1522, 1333, 1167. ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 0.89 (*t*, $J = 7.0$, 6 H); 1.11 (*s*, 3 H); 1.12 (*s*, 18 H); 1.15 (*s*, 3 H); 1.16 (*s*, 18 H); 1.30 (*m*, 36 H); 1.57 (*m*, 4 H); 3.29 (*t*, $J = 8.0$, 4 H); 6.54 (*d*, $J = 9.0$, 2 H); 7.32 (*d*, $J = 9.0$, 2 H); 7.60 (*d*, $J = 9.0$, 2 H); 8.20 (*d*, $J = 9.0$, 2 H). ^{13}C-NMR (50.3 MHz, $\mathrm{CDCl_3}$): 11.3; 11.4; 11.5; 14.1; 18.5; 18.7; 18.8; 22.7; 27.1; 27.2; 29.4; 29.5; 29.7; 31.9; 51.0; 87.2; 93.3; 94.6; 102.0; 102.1; 103.3; 104.0; 107.7; 111.1; 112.9; 120.3; 123.5; 130.0; 132.3; 133.6; 147.0; 148.7. FAB-MS: 985 (M^+). Anal. calc. for $\mathrm{C_{64}H_{100}N_2O_2Si_2}$ (985.69): C 77.99, H 10.23, N 2.84; found: C 77.93, H 10.01, N 2.56.

(Z)-1-[4-(Dimethylamino)phenyl]-6-(4-nitrophenyl)-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**46**). A soln. of **44** (80 mg, 0.12 mmol) in $\mathrm{Et_2O}$ (200 ml) was irradiated (366 nm) in a quartz flask for 2 h at r.t. Removal of the solvent and CC ($\mathrm{SiO_2}$-*H*, hexane/$\mathrm{Et_2O}$ 10:1) yielded **46** (30 mg, 37%) and recovered **44** (49 mg). R_f 0.25. Dark-red solid. M.p. 182–183°. UV/VIS ($\mathrm{CHCl_3}$): 295 (29900), 371 (30700), 471 (17000). IR ($\mathrm{CCl_4}$): 2181, 2143, 1606, 1522, 1342. ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$): 1.14 (*s*, 21 H); 1.15 (*s*, 21 H); 3.03 (*s*, 6 H); 6.65 (*d*, $J = 8.8$, 2 H); 7.35 (*d*, $J = 8.8$, 2 H); 7.63 (*d*, $J = 8.6$, 2 H); 8.21 (*d*, $J = 8.6$, 2 H). ^{13}C-NMR (125.8 MHz, $\mathrm{CDCl_3}$): 11.29; 18.68; 40.08; 87.35; 93.53; 95.14; 102.12; 102.41; 103.09; 103.20; 103.64; 108.79; 111.69; 113.15; 119.88; 123.66; 129.99; 132.19; 133.09; 147.10; 150.76. EI-MS (70 eV): 677 (100, M^+). HR-MS: 676.3889 (M^+, $\mathrm{C_{42}H_{56}N_2O_2Si_2^+}$; calc. 676.3880). X-Ray: [13].

*(E)-3,4-Bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-1,6-bis[4-(dimethylamino)phenyl]hex-3-ene-1,5-diyne* (**48**). A mixture of **47** (0.542 g, 1.49 mmol), *p*-iodo-*N,N*-dimethylaniline (0.736 g, 2.98 mmol), $[\mathrm{PdCl_2(PPh_3)_2}]$ (60 mg, 0.086 mmol), and CuI (30 mg, 0.16 mmol) in degassed $\mathrm{Et_3N}$ (60 ml) was stirred at r.t. for 24 h. Workup and CC ($\mathrm{SiO_2}$, hexane/$\mathrm{CH_2Cl_2}$ 3:1, then $\mathrm{CH_2Cl_2}$) gave **48** (0.351 g, 39%). R_f 0.2. Yellow solid. M.p. 166–167°. UV/VIS ($\mathrm{CHCl_3}$): 295 (15000), 380 (58400), 397 (sh, 51400). IR ($\mathrm{CCl_4}$): 3094, 3041, 2195, 1605, 1521, 1364, 1249. ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 0.17 (*s*, 12 H); 0.97 (*s*, 18 H); 3.00 (*s*, 12 H); 4.64 (*s*, 4 H); 6.66 (*d*, $J = 9.0$, 4 H); 7.35 (*d*, $J = 9.0$, 4 H). ^{13}C-NMR (75.5 MHz, $\mathrm{CDCl_3}$): –4.94; 18.54; 26.06; 40.23; 64.04; 85.66; 101.94; 110.54; 111.81; 128.20; 132.55; 150.07. EI-MS (70 eV): 603 (19, M^+), 546 (100, $[M - (t\text{-Bu})]^+$). Anal. calc. for $\mathrm{C_{36}H_{54}N_2O_2Si_2}$ (603.01): C 71.71, H 9.03, N 4.65; found: C 71.83, H 9.18, N 4.56. X-Ray: [13].

*(E)-3,4-Bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-1-(trimethylsilyl)hex-3-ene-1,5-diyne* (**49**). To a soln. of **47** (2.00 g, 5.49 mmol) in dry THF (200 ml) at −78° was added slowly 1.6M BuLi in hexane (3.8 ml, 6.08 mmol). After warming to −20° within 30 min, $\mathrm{Me_3SiCl}$ (1.1 ml, 8.72 mmol) was added, and the soln. was warmed up to r.t. within 1 h. Sat. aq. $\mathrm{NH_4Cl}$ soln. (20 ml) and hexane (300 ml) were added, and the mixture was extracted with $\mathrm{H_2O}$ (4 × 200 ml) and sat. aq. NaCl soln. (200 ml). After drying and removal of the solvent *in vacuo*, CC ($\mathrm{SiO_2}$, hexane/$\mathrm{CH_2Cl_2}$ 2:1) gave **49** (1.10 g, 46%). R_f 0.7. Pale-yellow oil. IR (film): 3313, 2957, 2141, 1252, 1100. ^{1}H-NMR (200 MHz, $\mathrm{CDCl_3}$): 0.09 (*s*, 12 H); 0.19 (*s*, 9 H); 0.90 (*s*, 18 H); 3.52 (*s*, 1 H); 4.42 (*s*, 2 H); 4.45 (*s*, 2 H). ^{13}C-NMR (50.3 MHz, $\mathrm{CDCl_3}$): –5.4; –0.5; 18.1; 25.6; 63.3; 63.7; 80.1; 88.6; 101.0; 106.5; 129.1; 131.1. EI-MS: 435 (0.3, M^+), 421 (4, $[M - \mathrm{CH_3}]^+$), 379 (100, $[M - (t\text{-Bu})]^+$), 73 (45, $[\mathrm{Me_3Si}]^+$). Anal. calc. for $\mathrm{C_{23}H_{44}O_2Si_3}$ (436.86): C 63.24, H 10.15; found: C 63.23, H 9.97.

*(E)-3,4-Bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-1-[4-(dimethylamino)phenyl]-6-(trimethylsilyl)hex-3-ene-1,5-diyne* (**50**). A mixture of **49** (0.025 g, 0.057 mmol), *p*-iodo-*N,N*-dimethylaniline (0.016 g, 0.065 mmol), $[\mathrm{PdCl_2(PPh_3)_2}]$ (3 mg, 0.004 mmol), and CuI (2 mg, 0.01 mmol) in degassed $\mathrm{Et_3N}$ (5 ml) was stirred at r.t. for 24 h. Workup and CC ($\mathrm{SiO_2}$-*H*, hexane/$\mathrm{CH_2Cl_2}$ 3:2) gave **50** (0.027 g, 85%). R_f 0.6. Yellow-brown solid. M.p. 64–65°. UV/VIS ($\mathrm{CHCl_3}$): 279 (sh, 15200), 292 (15900), 366 (35700). IR ($\mathrm{CCl_4}$): 3095, 3041, 2191, 2132, 1609, 1521, 1362, 1250. ^{1}H-NMR (200 MHz, $\mathrm{CDCl_3}$): 0.117 (*s*, 6 H); 0.121 (*s*, 6 H); 0.21 (*s*, 9 H); 0.92 (*s*, 9 H); 0.93 (*s*, 9 H); 2.97 (*s*, 6 H); 4.52 (*s*, 2 H); 4.53 (*s*, 2 H); 6.63 (*d*, $J = 9.0$, 2 H); 7.23 (*d*, $J = 9.0$, 2 H). ^{13}C-NMR (50.3 MHz, $\mathrm{CDCl_3}$): −5.07; −0.07; 18.44; 25.97; 40.13; 63.93; 64.26; 85.00; 102.41; 103.13; 105.66; 110.05; 111.71; 127.10; 131.51; 132.61; 150.17. EI-MS (70 eV): 556 (13, M^+), 73 (100, $[\mathrm{Me_3Si}]^+$). Anal. calc. for $\mathrm{C_{31}H_{53}NO_2Si_3}$ (556.03): C 66.97, H 9.61, N 2.55; found: C 66.71, H 9.52, N 2.43.

*(E)-3,4-Bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-1-[4-(dimethylamino)phenyl]-6-(4-nitrophenyl)hex-3-ene-1,5-diyne* (**51**). A mixture of **50** (0.040 g, 0.072 mmol) and $\mathrm{K_2CO_3}$ (35 mg, 0.25 mmol) in wet THF (5 ml) and MeOH (15 ml) was stirred at r.t. for 2 h. $\mathrm{Et_2O}$ and $\mathrm{H_2O}$ were added, the org. phase was separated, dried, reduced to 5 ml, and added to $\mathrm{Et_3N}$ (35 ml). The soln. was degassed, *p*-iodonitrobenzene (0.018 g, 0.072 mmol), $[\mathrm{PdCl_2(PPh_3)_2}]$ (5 mg, 0.007 mmol), and CuI (2 mg, 0.011 mmol) were added, and the mixture was stirred at r.t. for 24 h. Workup and CC ($\mathrm{SiO_2}$-*H*, hexane/$\mathrm{CH_2Cl_2}$ 2:1) gave **51** (0.034 g, 78%). R_f 0.25. Red solid. M.p. 149–150°. UV/VIS ($\mathrm{CHCl_3}$): 330 (25900), 424 (25000). IR ($\mathrm{CCl_4}$): 3094, 2172, 2159, 1608, 1521,

1340. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.13 (*s*, 6 H); 0.14 (*s*, 6 H); 0.92 (*s*, 18 H); 2.98 (*s*, 6 H); 4.59 (*s*, 2 H); 4.62 (*s*, 2 H); 6.64 (*d*, $J = 8.9$, 2 H); 7.34 (*d*, $J = 8.9$, 2 H); 7.55 (*d*, $J = 9.0$, 2 H); 8.18 (*d*, $J = 9.0$, 2 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): −5.15; 18.38; 25.86; 40.06; 63.97; 64.33; 85.39; 92.95; 98.05; 104.59; 109.69; 111.80; 112.07; 123.74; 126.32; 130.53; 131.94; 132.86; 146.96; 150.53. EI-MS (70 eV): 606 (6, M^+), 73 (100, $[Me_3Si]^+$). HR-MS: 604.3173 (M^+, $C_{34}H_{48}N_2O_4Si_2^+$; calc. 604.3152).

*(3*E*,9*E*)-1,12-Bis[4-(dimethylamino)phenyl]-3,4,9,10-tetrakis[(triisopropylsilyl)ethynyl]dodeca-3,9-diene-1,5,7,11-tetrayne* (**52**), *(3*E*,9*E*)-1,12-Bis(4-nitrophenyl)-3,4,9,10-tetrakis[(triisopropylsilyl)ethynyl]dodeca-3,9-diene-1,5,7,11-tetrayne* (**53**), *and (3*E*,9*E*)-1-[4-(dimethylamino)phenyl]-12-(4-nitrophenyl)-3,4,9,10-tetrakis[(triisopropylsilyl)ethynyl]dodeca-3,9-diene-1,5,7,11-tetrayne* (**54**). To a soln. of **41** (88 mg, 0.16 mmol) and **43** (84 mg, 0.15 mmol) in $CHCl_3$ (5 ml), open to the air, were added TMEDA (0.1 ml, 1.1 mmol) and CuCl (50 mg, 0.51 mmol), and the mixture was stirred for 2 h. Removal of the solvent *in vacuo* and CC (SiO_2-*H*, hexane/CH_2Cl_2 3:1) gave **52** (20 mg, 11%), **53** (28 mg, 16%), and **54** (40 mg, 23%).

52: R_f 0.4. Dark-red solid. M.p. 267–268° (dec.). UV/VIS ($CHCl_3$): 288 (44800), 355 (20800), 486 (45100). IR (CCl_4): 3096, 2942, 2183, 2142, 1605, 1518. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.10 (*s*, 42 H); 1.20 (*s*, 42 H); 2.99 (*s*, 12 H); 6.59 (*d*, $J = 9.0$, 4 H); 7.33 (*d*, $J = 9.0$, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.25; 11.32; 18.63; 18.70; 40.08; 82.40; 83.50; 87.15; 101.88; 102.33; 102.59; 103.42; 103.58; 109.02; 111.48; 113.84; 121.83; 133.30; 150.60. FAB-MS: 1110 (13, M^+), 59 (100). Anal. calc. for $C_{72}H_{104}N_2Si_4$ (1109.99): C 77.91, H 9.44, N 2.52; found: C 78.02, H 9.26, N 2.59.

53: R_f 0.5. Orange solid. M.p. 230° (dec.). UV/VIS ($CHCl_3$): 314 (47900), 430 (47600), 456 (sh, 41600). IR (CCl_4): 2194, 2147, 1612, 1527, 1341. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.08 (*s*, 6 H); 1.09 (*s*, 36 H); 1.11 (*s*, 6 H); 1.14 (*s*, 36 H); 7.61 (*d*, $J = 9.0$, 4 H); 8.21 (*d*, $J = 9.0$, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 11.21; 18.62; 83.25; 83.39; 91.67; 97.40; 101.45; 102.28; 104.57; 105.30; 117.86; 120.28; 123.55; 129.10; 132.52; 147.49. EI-MS (70 eV): 1114 (1, M^+), 59 (100). Anal. calc. for $C_{68}H_{92}N_2O_4Si_4$ (1113.84): C 73.33, H 8.33, N 2.52; found: C 73.25, H 8.43, N 2.52.

54: R_f 0.4. Dark-red solid. M.p. 264–265° (dec.). UV/VIS ($CHCl_3$): 293 (36700), 434 (27800), 481 (31300). IR (CCl_4): 2177, 2136, 1601, 1522, 1340. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.05 (*s*, 3 H); 1.06 (*s*, 18 H); 1.10 (*s*, 9 H); 1.11 (*s*, 54 H); 2.99 (*s*, 6 H); 6.59 (*d*, $J = 9.1$, 2 H); 7.32 (*d*, $J = 9.1$, 2 H); 7.58 (*d*, $J = 8.9$, 2 H); 8.18 (*d*, $J = 8.9$, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 11.22; 11.31; 18.62; 18.70; 40.09; 81.66; 82.36; 84.18; 84.79; 87.27; 91.91; 97.00; 101.71; 102.07; 102.29; 102.35; 102.93; 103.50; 104.08; 104.11; 104.90; 108.83; 111.49; 113.28; 118.34; 119.55; 122.57; 123.52; 129.29; 132.48; 133.39; 147.39; 150.70. FAB-MS: 1111 (14, M^+), 59 (100). HR-MS: 1110.6682 (M^+, $C_{70}H_{98}N_2O_2Si_4^+$; calc. 1110.6705).

Synthesis of **52** via *Oxidative Coupling of* **41**. A soln. of **41** (47 mg, 0.085 mmol), TMEDA (0.05 ml, 0.5 mmol), and CuCl (25 mg, 0.25 mmol), open to the air, was stirred for 2 h. The solvent was removed *in vacuo* and CC (SiO_2-*H*, hexane/CH_2Cl_2 3:1) gave **52** (25 mg, 53%).

*(3*E*,9*E*)-3,4,9,10-Tetrakis{[(*tert*-butyl)dimethylsilyloxy]methyl}-1,12-bis[4-(dimethylamino)phenyl]-dodeca-3,9-diene-1,5,7,11-tetrayne* (**55**). A mixture of **50** (0.040 g, 0.072 mmol) and K_2CO_3 (10 mg, 0.07 mmol) in wet THF (3 ml) and MeOH (10 ml) was stirred at r.t. for 2 h. Et_2O and H_2O were added, the org. phase was separated, dried, reduced to 3 ml, and added to 1,2-dichlorobenzene (5 ml). *Hay* catalyst (1.5 ml of $CHCl_3$, 0.05 ml of TMEDA, 15 mg of CuCl) was added, and the mixture was stirred, open to the air, at r.t. for 2 h. Evaporation *in vacuo* and CC (SiO_2-*H*, $CHCl_2$/hexane 3:1) afforded **55** (22 mg, 63%). R_f 0.2. Yellow solid. M.p. 153–155°. UV/VIS ($CHCl_3$): 297 (29700), 416 (68300). IR (CCl_4): 3095, 3044, 2174, 2118, 1608, 1518, 1359, 1251, 1121. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.11 (*s*, 12 H); 0.12 (*s*, 12 H); 0.91 (*s*, 18 H); 0.92 (*s*, 18 H); 2.98 (*s*, 12 H); 4.51 (*s*, 4 H); 4.55 (*s*, 4 H); 6.62 (*d*, $J = 9.0$, 4 H); 7.31 (*d*, $J = 9.0$, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): −5.05; 18.45; 25.97; 40.15; 63.97; 64.31; 82.60; 85.07; 85.54; 105.27; 109.81; 111.72; 126.17; 132.73; 133.93; 150.32. FAB-MS: 964 (28, M^+), 73 (100, $[Me_3Si]^+$). HR-MS: 964.5827 (M^+, $C_{56}H_{88}N_2O_4Si_4^+$; calc. 964.5821). Anal. calc. for $C_{56}H_{88}N_2O_4Si_4$ (965.68): C 69.65, H 9.19, N 2.90; found: C 69.40, H 9.34, N 2.77.

1-(4-Nitrophenyl)-6-(triisopropylsilyl)-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**57**). A mixture of **56** (0.20 g, 0.30 mmol) and K_2CO_3 (10 mg, 0.07 mmol) in wet THF (5 ml) and MeOH (20 ml) was stirred at r.t. for 2 h. Et_2O and H_2O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et_3N (40 ml). The soln. was degassed, *p*-iodonitrobenzene (0.075 g, 0.30 mmol), $[PdCl_2(PPh_3)_2]$ (20 mg, 0.029 mmol), and CuI (10 mg, 0.053 mmol) were added, and the mixture was stirred at r.t. for 18 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 2:1) gave **57** (163 mg, 76%). R_f 0.6. Light-yellow solid. M.p. 90–91°. UV/VIS ($CHCl_3$): 310 (24400), 359 (sh, 20700), 383 (24200). IR (neat): 2211, 2150, 1593, 1522, 1342. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.065 (*s*, 3 H); 1.07 (*s*, 18 H); 1.09 (*s*, 21 H); 1.097 (*s*, 3 H); 1.10 (*s*, 18 H); 7.55 (*d*, $J = 9.0$, 2 H); 8.17 (*d*, $J = 9.0$, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 11.20; 18.60; 92.35; 95.21; 102.66; 102.95; 103.46; 103.54; 103.80; 103.87; 116.08; 118.69; 123.49; 129.48; 132.34; 147.27. EI-MS (70 eV): 713 (100, M^+). Anal. calc. for $C_{43}H_{67}NO_2Si_3$ (714.28): C 72.31, H 9.45, N 1.96; found: C 72.15, H 9.27, N 1.98.

1-(4-Nitrophenyl)-6-phenyl-3,4-bis(phenylethynyl)hex-3-ene-1,5-diyne (**58**). A mixture of **57** (70 mg, 0.098 mmol) and Bu_4NF (0.35 ml, 1M in THF) in wet THF (10 ml) was stirred at r.t. for 0.5 h. Et_2O and H_2O were added, the org. phase was separated, dried, reduced to 5 ml, and added to Et_3N (20 ml). The soln. was degassed, iodobenzene (61 mg, 0.30 mmol), $[PdCl_2(PPh_3)_2]$ (10 mg, 0.014 mmol), and CuI (5 mg, 0.026 mmol) were added, and the mixture was stirred at r.t. for 24 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 10:1) gave **58** (7 mg, 15%). R_f 0.3. Red solid. M.p. 155–156° (dec.). UV/VIS ($CHCl_3$): 288 (sh, 22700), 304 (25000), 340 (24600), 418 (22100). IR (CCl_4): 3057, 2219, 2206, 2183, 1592, 1522, 1342. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.37 (*m*, 9 H); 7.56 (*m*, 6 H); 7.67 (*d*, *J* = 8.9, 2 H); 8.20 (*d*, *J* = 8.9, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 86.78; 87.19; 87.29; 92.13; 96.07; 99.67; 99.75; 100.18; 116.00; 119.09; 122.28; 122.31; 123.71; 128.49; 128.57; 129.30; 129.39; 129.45; 131.71; 131.76; 131.87; 132.38; 147.37. FAB-MS (70 eV): 473 (26, M^+), 109 (100%). HR-MS: 473.1413 (M^+, $C_{34}H_{19}NO_2^+$; calc. 473.1416).

*(*E*)- and (*Z*)-3-[(Bromo)(tributylstannyl)methylidene]-1-(triethylsilyl)-5-(trimethylsilyl)penta-1,4-diyne* (**64**). To **63** (1.00 g, 2.38 mmol) in dry THF (25 ml) at −78° was added dropwise 1.6M BuLi in hexane (1.5 ml, 2.4 mmol), and the mixture was stirred at −78° for 1 h. After addition of Bu_3SnCl (0.78 g, 2.4 mmol), the soln. was warmed to r.t., stirred overnight, quenched with sat. aq. NH_4Cl soln., and extracted with hexane. The org. phase was washed with sat. aq. NaCl soln., dried, and evaporated, after which CC (SiO_2, hexane) yielded **64** (1.20 g, 80%) as a 3:1 ratio of isomers (^{1}H-NMR). R_f 0.6. Yellow oil. IR (neat): 2955, 2150, 2111, 1463, 1249, 1017. ^{1}H-NMR (200 MHz, $CDCl_3$): major isomer: 0.21 (*s*, 9 H); 0.67 (*m*, 6 H); 0.91 (*t*, *J* = 7.2, 9 H); 1.03 (*q*, *J* = 6.8, 9 H); 1.18 (*m*, 6 H); 1.34 (*sext.*, *J* = 7.2, 6 H); 1.56 (*m*, 6 H); minor isomer: 0.24 (*s*, 9 H); 0.67 (*m*, 6 H); 0.89 (*t*, *J* = 7.2, 9 H); 1.03 (*q*, *J* = 6.8, 9 H); 1.18 (*m*, 6 H); 1.32 (*sext.*, *J* = 7.2, 6 H); 1.56 (*m*, 6 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): major isomer: −0.25; 4.51; 7.60; 12.4 (^1J(Sn,C) = 177.0, 169.1); 13.8; 25.5 (^2J(Sn,C) = 31.2); 29.0 (^3J(Sn,C) = 10.1); 95.2; 97.9; 102.9; 103.2; 120.8; 154.2; minor isomer: −0.73; 4.41; 7.52; 12.4 (^1J(Sn,C) = 177.0, 169.1); 13.8; 25.5 (^2J(Sn,C) = 31.2); 29.0 (^3J(Sn,C) = 10.1); 93.6; 99.1; 102.1; 104.3; 120.8; 153.9. EI-MS (70 eV): 573 ($[M - Bu]^+$).

*(*E*)- and (*Z*)-3-(Tributyltin)-6-(triethylsilyl)-1-(triisopropylsilyl)-4-[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**65**). To a degassed soln. of an isomeric (3:1) mixture of **64** (1.11 g, 1.76 mmol) and $(i\text{-}Pr)_2EtN$ (0.89 g, 6.9 mmol) in benzene (100 ml) was added $(i\text{-}Pr)_3Si{-}C{\equiv}CH$ (0.47 g, 2.6 mmol), $[PdCl_2(PPh_3)_2]$ (119 mg, 0.17 mmol), and CuI (32 mg, 0.17 mmol). The mixture was stirred for 4 d at r.t., then diluted with hexane and quenched with 0.1M HCl. The org. layer was washed with H_2O, sat. aq. $NaHCO_3$ soln., dried, and evaporated *in vacuo*. CC (SiO_2, hexane) gave **65** as *ca.* 3:2 mixture (^{1}H-NMR; 979 mg, 76%) of inseparable isomers. R_f 0.4. Pale-yellow oil. IR (neat): 2956, 2147, 2096, 1464, 1250, 1227. ^{1}H-NMR (200 MHz, $CDCl_3$): major isomer: 0.20 (*s*, 9 H); 0.67 (*m*, 6 H); 0.89 (*t*, *J* = 7.2, 9 H); 1.01 (*m*, 9 H); 1.10 (*s*, 21 H); 1.14 (*m*, 6 H); 1.31 (*m*, 6 H); 1.53 (*m*, 6 H); minor isomer: 0.19 (*s*, 9 H); 0.67 (*m*, 6 H); 0.89 (*t*, *J* = 7.2, 9 H); 1.01 (*m*, 9 H); 1.10 (*s*, 21 H); 1.14 (*m*, 6 H); 1.31 (*m*, 6 H); 1.53 (*m*, 6 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): major isomer: −0.67; 4.10; 7.16; 11.0; 11.2; 13.4; 18.5; 27.1; 28.7; 95.4; 96.5; 103.7; 105.2; 108.8; 111.4; 121.9; 147.0; minor isomer: −0.52; 4.10; 7.16; 11.0; 11.2; 13.4; 18.5; 27.1; 28.7; 95.2; 97.3; 102.6; 106.2; 108.9; 111.4; 122.1; 146.8. EI-MS (70 eV): 675 ($[M - Bu]^+$). Anal. calc. for $C_{38}H_{72}Si_3Sn$ (731.94): C 62.36, H 9.92; found: C 62.55, H 10.10.

*(*E*)- and (*Z*)-3-Iodo-6-(triethylsilyl)-1-(triisopropylsilyl)-4-[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**66**). An isomeric mixture (3:2) of **65** (0.896 g, 1.22 mmol) was added to a soln. of I_2 (0.373 g, 1.47 mmol) in dry Et_2O (50 ml), and the soln. was stirred for 14 h, then poured into hexane (50 ml) and H_2O (50 ml). The org. phase was separated, washed with H_2O (2×), dried, and concentrated *in vacuo*. CC (SiO_2, hexane) gave **66** (0.693 g, 99%) as an inseparable 1:1.1 mixture (^{1}H-NMR) of isomers. R_f 0.3. Pale-yellow oil. IR (neat): 2957, 2156, 2122, 1463, 1250, 1116. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 0.24 (*s*, 9 H); 0.65 (*m*, 6 H); 1.00 (*t*, *J* = 7.8, 9 H); 1.11 (*s*, 21 H); minor isomer: 0.20 (*s*, 9 H); 0.65 (*m*, 6 H); 1.00 (*t*, *J* = 7.8, 9 H); 1.11 (*s*, 21 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): major isomer: −0.42; 4.16; 7.44; 11.3; 18.6; 89.8; 99.5; 101.4; 104.8; 105.2; 107.3; 109.3; 120.0; minor isomer: −0.42; 4.16; 7.44; 11.3; 18.6; 89.6; 100.3; 101.3; 103.1; 106.0; 107.3; 108.9; 120.2. EI-MS (70 eV): 568 (M^+). Anal. calc. for $C_{26}H_{45}ISi_3$ (568.80): C 54.90, H 7.97; found: C 55.18, H 8.05.

*(*E*)- and (*Z*)-1-[4-(nitrophenyl)ethynyl]-6-(triethylsilyl)-3-(triisopropylsilyl)-4-[(trimethylsilyl)ethynyl]-hex-3-ene-1,5-diyne* (**67** and **68**). A 1:1.1 isomeric mixture of **66** (0.250 g, 0.440 mmol), *p*-ethynylnitrobenzene (0.097 g, 0.659 mmol), $[PdCl_2(PPh_3)_2]$ (20 mg, 0.029 mmol), and CuI (10 mg, 0.05 mmol) were added to degassed Et_3N (25 ml) and stirred at r.t. for 16 h. Workup and CC (SiO_2-*H*, hexane/CH_2Cl_2 15:1) gave **67** (0.109 g, 42%) and **68** (0.071 g, 28%).

67: R_f 0.15. Yellow solid. M.p. 94–95°. UV/VIS ($CHCl_3$): 311 (24500), 382 (24900). IR (CCl_4): 2944, 2111, 2148, 1589, 1520, 1339, 1250. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.20 (*s*, 9 H); 0.67 (*q*, *J* = 8.1, 6 H); 0.98 (*t*, *J* = 8.1, 9 H); 1.11 (*s*, 21 H); 7.58 (*d*, *J* = 9.1, 2 H); 8.19 (*d*, *J* = 9.1, 2 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): −0.58; 4.15; 7.30; 11.07; 18.56; 92.14; 95.57; 101.19; 102.46; 102.71; 103.54; 104.17; 106.33; 117.31; 118.99; 123.60; 129.53; 132.45; 147.47. EI-MS (70 eV): 587 (100, M^+). Anal. calc. for $C_{34}H_{49}NO_2Si_3$ (588.02): C 69.45, H 8.40, N 2.38; found: C 69.63, H 8.67, N 2.32.

68: R_f 0.13. Yellow solid. M.p. 66–68°. UV/VIS ($CHCl_3$): 311 (24000), 383 (25800). IR (CCl_4): 2955, 2210, 2148, 1589, 1520, 1339, 1250. ^1H-NMR (200 MHz, $CDCl_3$): 0.21 (*s*, 9 H); 0.64 (*q*, $J = 8.1$, 6 H); 1.00 (*t*, $J = 8.1$, 9 H); 1.10 (*s*, 21 H); 7.57 (*d*, $J = 8.7$, 2 H); 8.19 (*d*, $J = 8.7$, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): −0.39; 4.09; 7.30; 11.14; 18.60; 92.36; 95.67; 101.66; 102.45; 102.46; 103.82; 104.84; 105.92; 117.28; 118.91; 123.72; 129.60; 132.49; 147.50. EI-MS (70 eV): 587 (100, M^+). (588.02): C 69.45, H 8.40, N 2.38; found: C 69.22, H 8.47, N 2.21.

N,N-*Didodecyl-4-[(trimethylsilyl)ethynyl]aniline* (**69**). A mixture of **27** (0.67 g, 1.2 mmol), $Me_3Si{-}C{\equiv}CH$ (0.20 g, 0.29 ml, 2.0 mmol), $[PdCl_2(PPh_3)_2]$ (42 mg, 0.06 mmol), and CuI (21 mg, 0.1 mmol) in degassed Et_3N (30 ml) was stirred at r.t. for 24 h. Workup gave **69** (0.57 g, 90%) as a light-yellow oil. IR (neat): 2904, 2144, 1605, 15.13, 1246. ^1H-NMR (200 MHz, $CDCl_3$): 0.26 (*s*, 9 H); 0.92 (*t*, $J = 6.4$, 6 H); 1.30 (br. *s*, 36 H); 1.58 (*m*, 4 H); 3.27 (*t*, $J = 6.8$, 4 H); 6.53 (*d*, $J = 8.9$, 2 H); 7.32 (*d*, $J = 8.9$, 2 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 0.24; 14.12; 22.71; 27.12; 27.18; 29.38; 29.52; 29.56; 31.61; 31.94; 50.90; 90.61; 106.84; 108.62; 110.96; 133.22; 147.99. EI-MS (70 eV): 526 (53, M^+), 73 (100, $[Me_3Si]^+$). Anal. calc. for $C_{35}H_{63}NSi$ (525.47): C 79.93, H 12.08, N 2.66; found: C 79.77, H 11.90, N 2.69.

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