DOI: 10.1002/ejoc.201000030

Chiral and Achiral Charge-Transfer Chromophores with a Dendralene-Type Backbone by Electronically Controlled Cycloaddition/Cycloreversion Cascades

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Keywords: Alkynes / Charge transfer / Chirality / Conjugation / Cycloaddition / Cascade reactions

Chiral and achiral push-pull chromophores have been prepared by cascades of sequential [2+2] cycloadditions of tetracyanoethene (TCNE) and tetrathiafulvalene (TTF) to different oligoynes. Thermal [2+2] cycloaddition of TCNE to donor-substituted alkynes, followed by electrocyclic ring-opening of the initially formed cyclobutenes, affords donor-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs). Similarly, TTF reacts with electron-deficient C≡C bonds to give the corresponding buta-1,3-diene derivatives, 1,2-bis(1,3-dithiol-2-ylidene)ethanes. Thus, achiral [AB]-type oligomers were synthesized from *N*,*N*-dialkylanilino (DAA)-substituted tetraynes and hexaynes and chiral [AB]-type oligomers from alkyne-substituted 1,1′-binaphthalenes. The [AB]-type oligomers exhibit complex conformational equilibria in solution, as revealed by ^{1}H and ^{13}C NMR spectroscopy. Therefore, the circular dichroism (CD) spectra of the chiral [AB]-type oligomers were measured to investigate whether a preferred conformation of the dendralene-type backbone is induced by the optically active 1,1′-binaphthalene moiety. Electrochemical studies by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV) showed large cathodic shifts of the first oxidation potentials for some of the chiral and achiral [AB]-type oligomers due to sterically enforced π-deconjugation of the acceptor and donor moieties. The new multivalent systems feature intense, bathochromically shifted intramolecular charge-transfer (CT) bands in the UV/Vis spectra. Extended, donor-substituted TCBDs, which are obtained by mono-addition of TCNE to the hexaynes, exhibit low optical and electrochemical HOMO–LUMO gaps. In addition, a large third-order optical nonlinearity was measured for one of these TCBDs by degenerate four-wave mixing (DFWM).

Introduction

The thermal [2+2] cycloaddition of tetracyanoethene (TCNE) to *N*,*N*-dialkylanilino (DAA)-substituted alkynes, followed by electrocyclic ring-opening of the initially formed cyclobutenes, has the character of a "click"-reaction, affording DAA-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs) in an atom-economic way and with near quantitative yields without the need for catalysis.[1–8] Donor-substituted alkynes also react with other electron-accepting olefins, such as 7,7,8,8-tetracyanoquinodimethanes (TCNQs),[9–13] dicyanovinyl (DCV) and tricyanovinyl derivatives,[14,15] with formation of non-planar donor-acceptor (D-A) chromophores with intense intramolecular charge-transfer (CT) interactions.[16] Some of the *N*,*N*-dimethylanilino (DMA)-substituted TCBDs exhibit high third-order polarizability,[3] and one of them {DDMEBT, 2-[4-(dimethylamino)phenyl]-3-[(4-dimethylamino)phenyl]-ethynylbuta-1,3-diene-1,1,4,4-tetracarbonitrile} was shown to form high-optical-quality, homogeneous thin films by vapor-phase deposition.[17] These films have found first applications as materials for integrated nonlinear optics (NLO).[18,19] In addition, TCBDs substituted with chiral, *N*-arylated dinaphthazepine donors have been used as dopants in nematic liquid crystals (LCs) featuring high helical twisting powers (HTP).[20]

Hopf et al. showed that a similar cycloaddition reaction also occurs under the conditions of inverse electron demand. They reported that the strong electron donor tetrathiafulvalene (TTF) reacts with electron-deficient C≡C bonds in cyanoethynylethenes to give the corresponding butadiene derivatives, 1,2-bis(1,3-dithiol-2-ylidene)ethanes.[21] This transformation has also been described by Hirsch and co-workers for α,ω-dicyanopolyynes.[22] A related cycloaddition/cycloreversion involving electron-deficient alkynes was reported earlier by Dolbier and co-workers.[23] Re-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201000030.

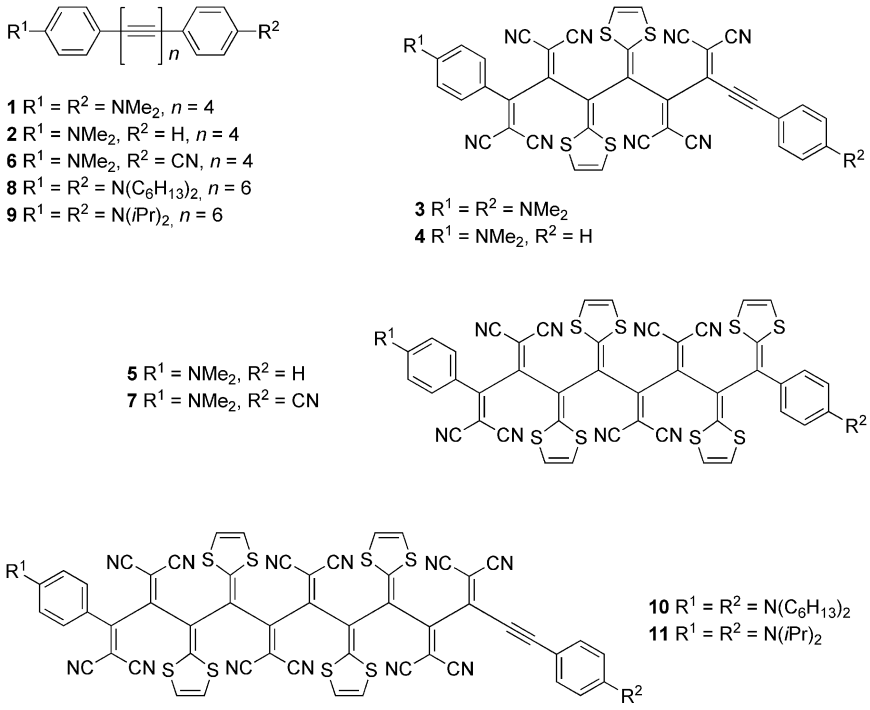


Figure 1. Conjugated [AB]-type oligomers and their oligoyne precursors.

cently, we combined the two electronically controlled cycloaddition reactions in a cascade of successive TCNE and TTF additions to end-capped tetraynes **1** and **2** (Figure 1).[24] After the first [2+2] cycloaddition of **1** and **2** with TCNE to give the corresponding TCBDs, the C≡C bond next to the TCBD moiety is sufficiently electron-deficient to undergo [2+2] cycloaddition with TTF in good yield. The regioselectivity of the next TCNE addition is determined by the 1,2-bis(1,3-dithiol-2-ylidene)ethane donor unit to give the A-D-A systems **3** and **4** in good to excellent yields (Figure 1). The remaining triple bond in **3** is not sufficiently electron-deficient to undergo [2+2] cycloaddition to TTF, whereas **4** reacted with TTF to give the [AB]-type oligomer **5** in 21% yield. The last CC triple bond in **4** is electron-deficient, while the one in **3** is "electronically confused", because of the substitution by both a donor (DMA) and an acceptor moiety (TCBD). Finally, a one-pot protocol for the cascade of successive TCNE/TTF cycloadditions to tetrayne **2** was shown to give **5** in 21% overall yield. From these results, we anticipated that replacing the phenyl moiety in **2** by an activating 4-cyanophenyl moiety in tetrayne **6** should lead to even higher yields in the one-pot cycloaddition cascade (Figure 1). We expected the new [AB]-type oligomer **7** as the sole product from this entirely electronically controlled transformation.

The *N*,*N*-dihexylanilino (DHA)-substituted hexayne **8** was recently obtained as a side product in the synthesis of new D-A-substituted oligoynes, which will be published elsewhere.[25] Together with its *N*,*N*-diisopropylanilino-substituted analogue **9**, oligoyne **8** is used here to synthesize the new extended [AB]-type oligomers **10** and **11** by a cascade of successive TCNE and TTF additions. Similar to the A-D-A system **3**, it was expected that the last, "electronically confused" triple bond in **10** and **11** will not react with TTF or TCNE.

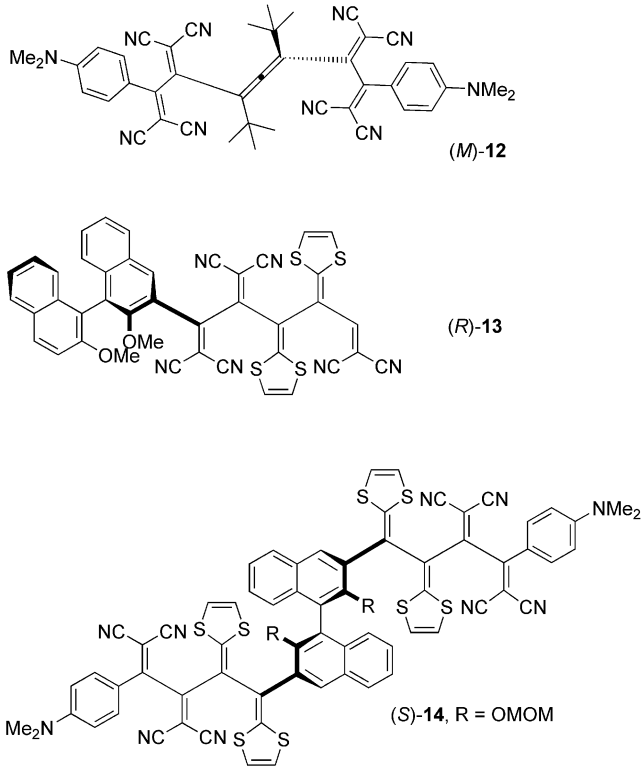


Figure 2. D-A-substituted 1,3-diethynylallene (*M*)-**12**,[26] and chiral [AB]-type oligomers (*R*)-**13** and (*S*)-**14**.

Complex conformational equilibria were observed for solutions ($C_2D_2Cl_4$) of [AB]-type oligomers **3**–**5** by ^1H and ^{13}C NMR spectroscopy.[24] Inspired by very recent results with donor-substituted 1,3-diethynylallenes (DEAs, Figure 2),[26,27] we assumed that the presence of a suitable chiral substituent may induce a preferred conformation of the dendralene-type backbone[28–30] in the [AB]-type oligomers. The circular dichroism (CD) spectrum of enantiopure DEA (*M*)-**12** showed Cotton effects associated with the CT absorptions of the TCBD. This clearly indicated chiral induction from the allene into the TCBD moieties,[26] which was confirmed in theoretical simulations of the CD spectrum.[27]

Encouraged by the high HTP values found for *N*-arylated dinaphthazepines, which constitute 2,2′-bridged 1,1′-binaphthalenes,[20] we decided to also use 1,1′-binaphthalene moieties as building blocks for induction of chirality into the new chiral [AB]-type oligomers (*R*)-**13** and (*S*)-**14** (Figure 2). The alkoxy substituents in the 2,2′-positions of (*R*)-**13** and (*S*)-**14** were expected to enforce strong conformational preferences and help achieving chiral induction into the dendralene-type backbone through intramolecular steric interactions. The conformational equilibria and the possible presence of preferred chiral conformers are investigated here by a combination of variable temperature (VT)-NMR and VT-CD spectroscopy.

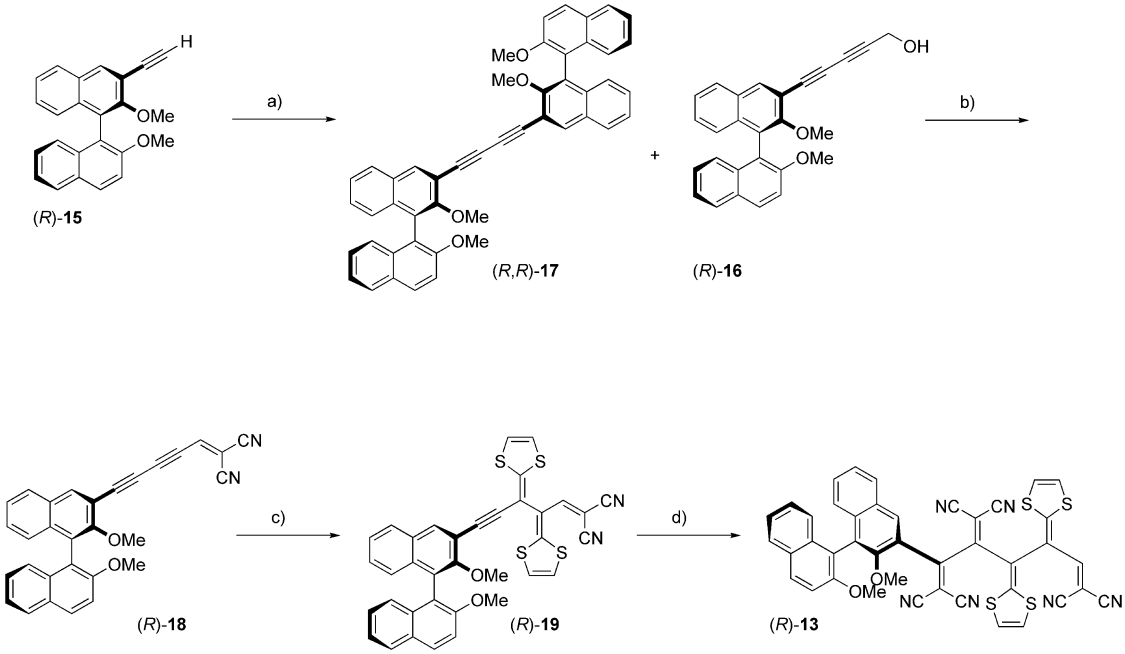
Results and Discussion

Synthesis of Chiral [AB]-Type Oligomer (*R*)-13

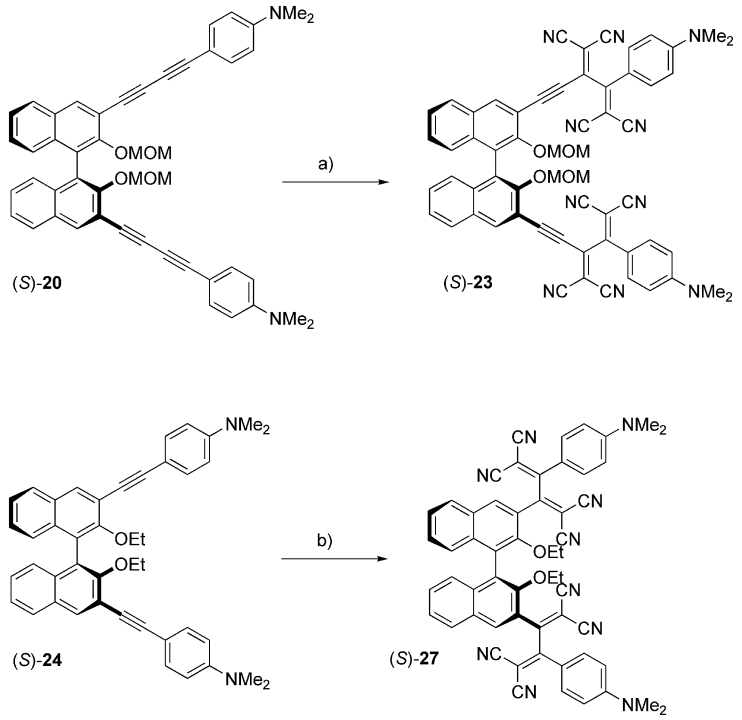
The synthesis of (*R*)-**13** started from alkyne (*R*)-**15**, which was prepared from (*R*)-1,1′-bi(2,2′-naphthol) [(*R*)-BINOL] according to a published procedure.[31,32] Oxidative Hay coupling with an excess of prop-2-yn-1-ol provided alcohol (*R*)-**16** in 51% yield together with buta-1,3-diyne (*R*,*R*)-**17** (18%, Scheme 1), formed by homo-coupling of (*R*)-**15**. A "one-pot" oxidation/Knoevenagel condensation protocol, starting from (*R*)-**16**, yielded the dicyanovinyl derivative (*R*)-**18** in 32%.[33] The dicyanovinyl group activates the adjacent C≡C bond in (*R*)-**18** for the cycloaddition reaction with TTF[21] to give, after cycloreversion, adduct (*R*)-**19** in 33% yield. Target compound (*R*)-**13** was subsequently obtained in 50% yield cycloaddition/cycloreversion of TCNE. The low yield in this transformation may be explained by the high degree of steric hindrance in (*R*)-**19**. The constitution of this chiral A-D-A system (A = acceptor, D = donor) was proven by the spectroscopic data (^1H NMR, MS, IR), although complex conformational equilibria complicate the interpretation of the ^1H NMR spectrum. VT-NMR spectroscopic experiments (–30 to 100 °C) were performed with a $C_2D_2Cl_4$ solution of (*R*)-**13** (see the Supporting Information). Similarly to the previously reported, achiral A-D-A derivatives **3** and **4**,[24] the coalescence of all signals was not observed in the ^1H NMR spectrum of (*R*)-**13** even at 80 to 100 °C. The temperature at which frozen conformations could be monitored by ^1H NMR spectroscopy was not reached due to the low solubility of (*R*)-**13**, which also prevented the recording of ^{13}C NMR spectra.

Synthesis of Chiral [AB]-Type Oligomers Based on 3,3′-Substituted 1,1′-Binaphthalenes

The bis(diyne) (*S*)-**20** was obtained by Sonogashira cross-coupling of 3,3′-diiodo-2,2′-bis(methoxymethoxy)-



Scheme 1. Synthesis of the chiral [AB]-type oligomer (*R*)-**13**. a) Prop-2-yn-1-ol, CuCl, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), CH_2Cl_2, 18 h, 25 °C, 51% [(*R*)-**16**], 18% [(*R*,*R*)-**17**]. b) 1. (*R*)-**16**, Dess–Martin periodinane, CH_2Cl_2, 1 h, 25 °C; 2. $CH_2(CN)_2$, Al_2O_3, CH_2Cl_2, 1 h, 50 °C, 32% (yield over two steps). c) TTF, MeCN/CH_2Cl_2, 1:1, 13 h, 50 °C, 33%. d) TCNE, CH_2Cl_2, 24 h, 25 °C, 50%.



Scheme 2. Synthesis of chiral CT-chromophores (*S*)-**23** and (*S*)-**27**. a) TCNE, TTF, MeCN/CH_2Cl_2, 3:1, 18 h, 50 °C, 29%. b) TCNE, CH_2Cl_2, 18 h, 25 °C, 70%.

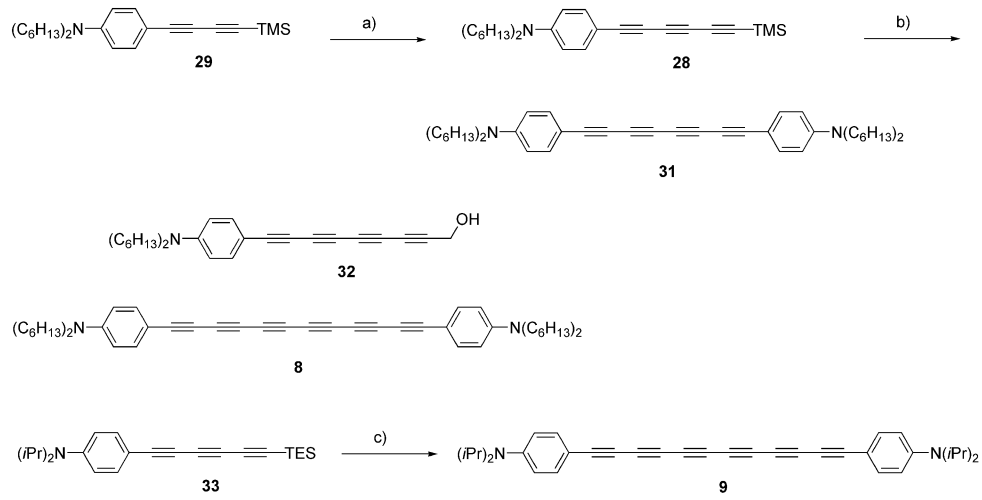
1,1′-binaphthyl [(*S*)-**21**][34] with 4-(buta-1,3-diyn-1-yl)-*N*,*N*-dimethylaniline (**22**)[4] (see the Supporting Information). With the precursor (*S*)-**20** in hands, we attempted the synthesis of the chiral [AB]-type oligomer (*S*)-**14** by the one-pot protocol for cascade TCNE/TTF additions (see above).[24] Interestingly, only the bis-TCNE adduct (*S*)-**23** was isolated in 29% overall yield when (*S*)-**20** was treated with an excess of TCNE and TTF in MeCN/CH_2Cl_2 at 50 °C (Scheme 2). The desired addition of TTF to the C≡C bonds directly attached to the naphthalene moieties may not occur for various reasons. These triple bonds are sterically blocked by the neighboring methoxymethoxy (OMOM) groups and the TCBD moieties, and in addition, they may not be sufficiently electron deficient to undergo [2+2] cycloadditions to TTF due to the electron-donating OMOM groups. These types of C≡C bonds have been described as "electronically confused" (see above).[24] The C_2-symmetric diyne (*S*)-**24** was prepared from (*S*)-3,3′-diiodo-2,2′-diethoxy-1,1′-binaphthyl [(*S*)-**25**][35] by twofold Sonogashira cross-coupling with 4-ethynyl-*N*,*N*-dimethylaniline (**26**)[36] (see the Supporting Information). The chiral CT-chromophore (*S*)-**27** was obtained in 70% yield (that is, 84% for each cycloaddition/cycloreversion step) by reaction of (*S*)-**24** with TCNE.

Synthesis of Precursors for Achiral [AB]-Type Oligomer

The precursor for *N*,*N*-dihexylanilino (DHA) substituted 1,3,5-hexatriyne **28** (Scheme 3), diyne **29**, was synthesized by oxidative Hay coupling of 4-ethynyl-*N*,*N*-dihexylaniline (**30**)[37] with (trimethylsilyl)acetylene (TMSA) (Supporting Information). Diyne **29** was then subjected to TMS-deprotection, followed by another Hay-type coupling reaction with an excess of TMSA to give the unsymmetric triyne **28** in 50% yield (Scheme 3). Tetrayne **31** was formed in 15% yield by homo-coupling of deprotected **29**. The use of an excess of TMSA leads to the preferred formation of the hetero-coupled product. Triyne **28** was found to be highly unstable as a solid and in solution; decomposition to an insoluble black residue was observed already at temperatures exceeding 40 °C. Therefore, evaporation of the solvents in vacuo was performed at 30 °C or lower.

During the synthesis of alcohol **32**, which is the precursor for a new D-A tetrayne,[25] hexayne **8** was isolated as a side product in 38% yield from homo-coupling of deprotected **28** (Scheme 3). Although a large excess (15 equiv.) of prop-2-yn-1-ol was employed in the oxidative coupling reaction, the homo-coupling product **8** was formed in slightly higher yield than the cross-coupling product **32**.[38] Separation of **8** and **32** by flash chromatography (FC) was straightforward due to the large difference in polarity between the alcohol and the hexayne. Like their precursor **28**, hexayne **8** and tetrayne **32** exhibit very low thermal stability and decomposition to black insoluble materials was observed at temperatures above 40 °C for solutions and in the solid state.

The analogue of **8** bearing *N*,*N*-diisopropylanilino residues instead of DHA donors was synthesized from the triethylsilyl (TES)-protected triyne **33** (Scheme 3). The use of diisopropylanilino substituents instead of DHA residues should facilitate crystal formation for X-ray analysis, while maintaining good solubility of hexayne **9** and the derived

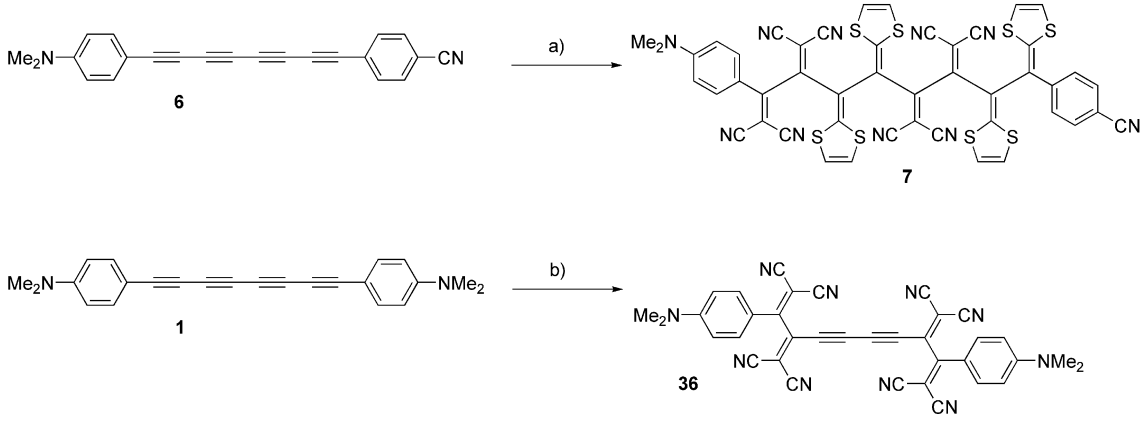


Scheme 3. Oxidative coupling reactions to synthesize donor-substituted oligoynes. a) 1. K_2CO_3, MeOH/THF, 1:1, 2 h, 25 °C; 2. (Trimethylsilyl)acetylene (TMSA), CuCl, TMEDA, acetone, 3 h, 25 °C, 50% (**28**, yield over two steps), 15% (**31**, yield over two steps). b) 1. **28**, K_2CO_3, MeOH/THF, 1:1, 1 h, 25 °C; 2. Prop-2-yn-1-ol, CuCl, TMEDA, CH_2Cl_2, 2 h, 25 °C, 38% (**8**, yield over two steps), 34% (**32**, yield over two steps). c) 1. nBu$_4$NF, THF, 20 min, 0 °C; 2. CuCl, TMEDA, CH_2Cl_2, 2 h, 25 °C, 65% (yield over two steps).

[AB]-type oligomers. The triyne **33** was prepared according to a known procedure (Supporting Information).[39] TES-deprotection with nBu$_4$NF, followed by oxidative Hay coupling, provided the desired hexayne **9** in 65% yield. Unambiguous proof of the formation of hexayne **9** was obtained by X-ray crystallographic analysis (see below). Octatetrayne **6** was obtained by oxidative Hay coupling of the TMS-deprotected diynes 4-[4-(trimethylsilyl)buta-1,3-diyn-1-yl]benzonitrile (**34**)[40] and 4-[4-(trimethylsilyl)buta-1,3-diyn-1-yl]-*N*,*N*-dimethylaniline (**35**)[4] (Supporting Information).

[2+2] Cycloadditions of Donor-Substituted Oligoynes with TCNE and TTF

We attempted the cascade of successive TCNE/TTF [2+2] cycloadditions to the mono-DMA, mono-(4-cyanophenyl)-substituted tetrayne **6** (Scheme 4). Reaction of **6** with an excess of TTF and TCNE in the one-pot setup furnished the [ABAB] system **7** in a significantly increased yield of 58% (that is, 87% per cycloaddition/cycloreversion sequence) as compared to **5** (21%, see above). This can be rationalized by comparing the Hammett constants of the phenyl substituent [σ_p(Ph) = –0.01][41] in **2** and the 4-cyanophenyl substituent [σ_p(CN) = +0.66][41] in **6**. The phenyl substituent acts as a very weak electron donor, contributing to the "electronic confusion" of the adjacent alkyne moiety. In **6**, this effect is completely eliminated by the electron-withdrawing 4-cyanophenyl moiety. As in the case of **3**, **4**, **5**, and (*R*)-**13** (see above), the NMR spectroscopic characterization of **7** was seriously complicated by the presence of complex conformational equilibria in solution. Reaction of the symmetric bis-donor-substituted tetrayne **1** with an excess of TCNE in CH_2Cl_2 afforded bisadduct **36** in 55% yield (Scheme 4). On the other hand, the same reaction with one equivalent of TCNE gives exclusively the monoadduct in 72% yield.[24] Only traces of the monoadduct were ob-



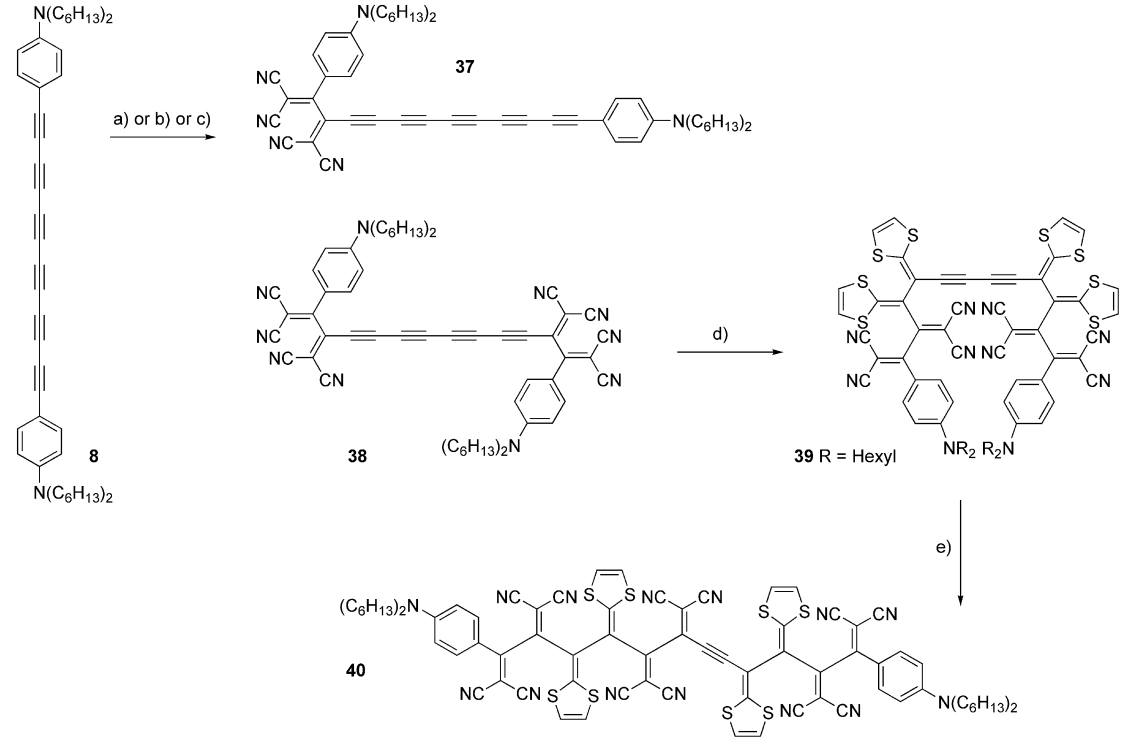
Scheme 4. [2+2] Cycloaddition/cycloreversion cascades. a) TCNE, TTF, CH_2Cl_2/MeCN, 1:1, 18 h, 50 °C, 58%. b) 2.9 equiv. TCNE, CH_2Cl_2, 17 h, 25 °C, 55%.

served in the synthesis of **36**. Chromophores **7** and **36** were obtained as black metallic-like solids, which are stable up to their melting points.

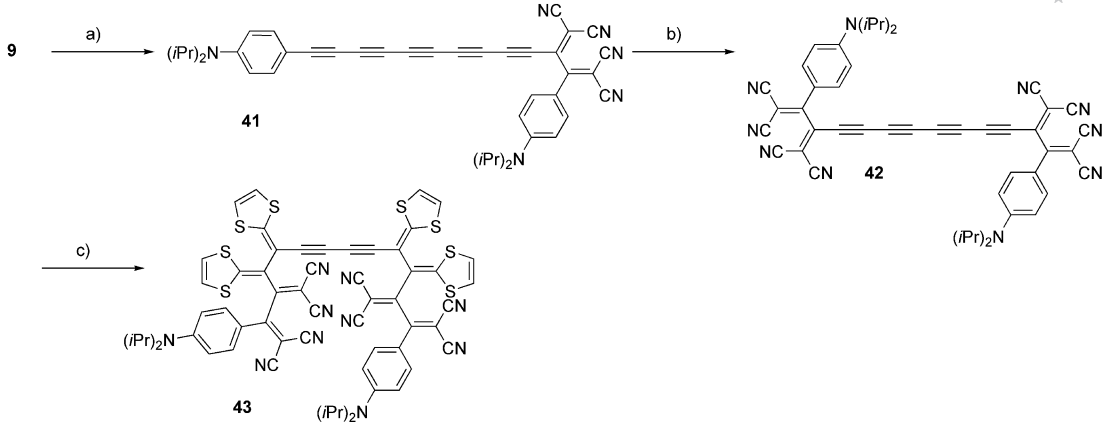
Hexayne **8** was used to access the extended version of [AB]-type oligomer **3** (see above).[24] Surprisingly, reaction of **8** with one equivalent of TCNE gave a 1:1 mixture of TCBD **37** (39% yield) and the symmetric bisadduct **38** (39% yield, Scheme 5). This result is in contrast to the observed reactivity for tetrayne **1** (see above).[24] It is assumed that the additional separation of the TCBD moiety from the reacting C≡C bond in **37** strongly reduces its electron-withdrawing effect. Thus, this triple bond remains sufficiently electron-rich in **37** to undergo the second TCNE addition after a short time without using an excess of TCNE. In the case of **1**, a prolonged reaction time and an excess of TCNE was necessary to obtain bisadduct **36** (see above). Monoadduct **37** can be selectively synthesized in 65% yield by using only 0.8 equiv. of TCNE in the [2+2] cycloaddition reaction with **8**. In this case, only traces of the bisadduct **38** were observed and it was possible to isolate unreacted **8** from the crude reaction mixture by FC. Similar to its precursors, pentayne **37** showed low thermal stability with decomposition reactions occurring at temperatures above 40 °C. Bisadduct **38** was selectively obtained in 88% yield by adding two equivalents of TCNE to **8**. This yield is higher than for bisadduct **36** (55%), which is in agreement with the observed difference in reactivity between tetrayne **1** and hexayne **8**. The symmetric tetrayne **38** is stable up to its melting point at 161–163 °C.

Alkynes **37** and **38** can be used to build up two different [AB]-type oligomers. One by a cascade of successive TTF/TCNE additions from one side of the pentayne to the other, starting from **37**. This reaction sequence leads to the analogue of **3**, [AB]-type oligomer **10** (see above). On the other hand, successive TTF/TCNE additions may also occur starting from both sides of the symmetric tetrayne **38**. This reaction sequence has not been investigated in the case of the tetrayne **1**. Thus, **38** was treated with an excess of TTF in CH_2Cl_2/MeCN, 1:1 to give the hybrid TCNE-TTF adduct **39** in 58% yield (Scheme 5). Finally, TCNE addition to **39** gave the [AB]-type oligomer **40** in 96% yield. The remaining C≡C bond in **40** is "electronically confused" and, therefore, does not react with TCNE or with TTF. Again, complex conformational equilibria in solution seriously complicate the interpretation of the ^1H and ^{13}C NMR spectra of **39** and **40**.[24] High-temperature ^1H NMR spectra were measured up to 80 °C for **39** and up to 100 °C for **40** (Supporting Information). Coalescence of the ^1H NMR signals was not observed under these conditions. [AB]-type oligomers **39** and **40** were obtained as brown solids, which are stable up to their melting points at 252–254 °C and 217–219 °C, respectively.

The one-pot protocol, which was successfully used in the synthesis of **5** and **7** (see above),[24] should give a 1:1 mixture of the constitutional isomers **10** and **40** in the case of the symmetric hexayne **8**. However, separation of the two isomers **10** and **40** by FC was not possible and, therefore, the one-pot protocol was not used with hexaynes **8** and **9**.



Scheme 5. Synthesis of [AB]-type oligomers **39** and **40**. a) **8**, 0.8 equiv. TCNE, CH_2Cl_2, 5 h, 25 °C, 65% (**37**). b) **8**, 1.0 equiv. TCNE, CH_2Cl_2, 3 h, 25 °C, 39% (**37**), 39% (**38**). c) **8**, 2.0 equiv. TCNE, CH_2Cl_2, 18 h, 25 °C, 88% (**38**). d) **38**, TTF, CH_2Cl_2/MeCN, 1:1, 6 h, 50 °C, 58%. e) 3.6 equiv. TCNE, CH_2Cl_2, 18 h, 25 °C, 96%.



Scheme 6. Synthesis of [AB]-type oligomer **43**. a) 0.7 equiv. TCNE, CH_2Cl_2, 5 h, 25 °C, 83%. b) 2.0 equiv. TCNE, CH_2Cl_2, 18 h, 25 °C, 65%. c) TTF, MeCN/CH_2Cl_2, 1:1, 4 h, 50 °C, 65%.

Hexayne **9** was selectively converted into the expanded TCBD **41** by [2+2] cycloaddition with 0.7 equiv. of TCNE (Scheme 6). The yield of **41** (83%) was further improved in comparison to **37** (65%, Scheme 5) by the use of 0.7 instead of 0.8 equiv. of TCNE. As described for **37**, unreacted **9** could be isolated after the reaction by FC. Twofold cycloaddition of TCNE to **9** was not observed under these conditions. The thermal stability of **9** and **41** was not investigated, as it is assumed that their stability is similar to that of **8** and **37**; therefore they were handled and stored at temperatures below 40 °C. TCNE addition to the electron-rich C≡C bond next to the diisopropylanilino residue in **41** gave **42** in 65% yield. Finally, **42** was treated with TTF to give the diisopropylanilino analogue of **39**, hybrid TCNE-TTF adduct **43**, in 65% yield. The [AB]-type oligomer **43** was obtained as a brown solid which decomposed upon melting at 205–208 °C. For the same reasons as described previously, the complex ^{1}H NMR spectrum of **43** is reported in the Experimental Section as empiric enumeration of observed signals. The ^{13}C NMR spectrum of **43** was not obtained due to the low solubility of the compound.

X-ray Structure and Bond Length Alternation in Hexayne 9

Single crystals of **9** were obtained by slow evaporation of a solution of **9** in CH_2Cl_2 at 25 °C (Figure 3). The crystals have the triclinic space group $\bar{P}1$. The bond angles at the C≡C triple bonds, which have values between 176° and 179° (see caption to Figure 3), indicate that the 1,3,5,7,9,11-dodecahexayne moiety is slightly bent. The molecule adopts a gentle S shape. A similar shape was recently found by Tykwinski et al. in the first crystallographic analysis of a decayne.[42] The two diisopropylanilino rings in **9** are

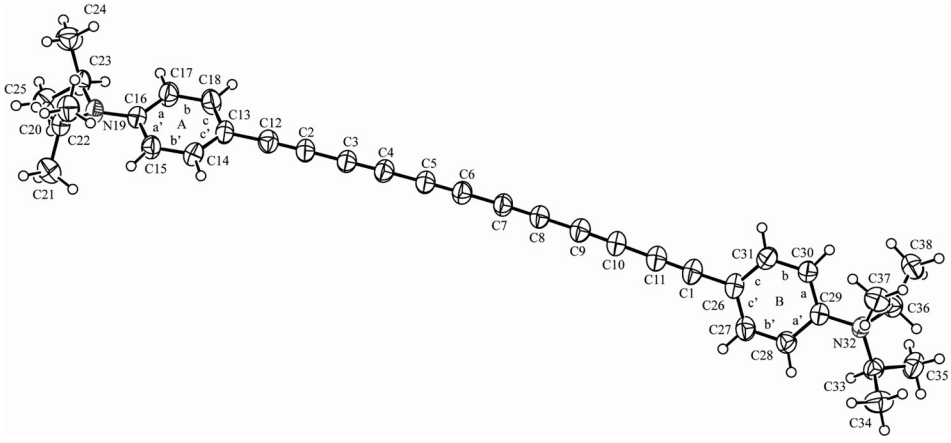


Figure 3. ORTEP plot of **9** at 203 K, arbitrary numbering. Atomic displacement parameters are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: C16–C17 1.410(3), C17–C18 1.379(3), C13–C18 1.397(4), C13–C14 1.395(3), C14–C15 1.380(3), C15–C16 1.410(3), N19–C16 1.382(3), C12–C13 1.419(3), C2–C12 1.214(3), C2–C3 1.354(3), C3–C4 1.220(3), C4–C5 1.352(3), C5–C6 1.210(3), C26–C27 1.400(4), C26–C31 1.403(4), C27–C28 1.372(3), C28–C29 1.411(3), C29–C30 1.411(3), C30–C31 1.365(3), C11–C1–C26 178.3(3), C12–C2–C3 176.7(3), C4–C3–C2 176.7(3), C3–C4–C5 178.2(3), C6–C5–C4 177.8(3), C5–C6–C7 179.1(3). Selected torsional angles [°]: dihedral angle between best planes through phenyl rings 56, N32–C29–C30–C31 176.9(2), C20–N19–C16–C15 22.1(3), C23–N19–C16–C15 –174.6(2), N19–C16–C17–C18 –176.6(3), C12–C13–C18–C17 176.5(3), C1–C26–C31–C30 –178.9(3). Quinoid character: δr = {[(a + a')/2 – (b + b')/2] + [(c + c')/2 – (b + b')/2]}/2.[44] δr = 0.024 and 0.038 for diisopropylanilino rings A and B, respectively.

twisted by ca. 56° with respect to each other (see caption to Figure 3). These findings can be explained by crystal packing forces. Tykwinski et al. reported a similar observation for the X-ray crystal structure of an aryl-substituted hexayne. They found the terminal aryl groups to be nearly orthogonal.[43] The arrangement of neighboring molecules in the crystal packing of **9** is shown in the Supporting Information.

The quinoid character of the diisopropylanilino rings (δr; for its definition[44] and bond lengths, see caption to Figure 3) in **9** was calculated to investigate the efficiency of the CT conjugation from the diisopropylanilino donors to the hexayne acceptor moiety. Compound **9** exhibits δr values of 0.024 and 0.038, for the two diisopropylaniline rings A and B, respectively. This is a large difference in δr values for two chemically identical donor substituents. The large difference in δr values for the two diisopropylanilino rings in **9** is most probably caused by crystal packing forces, which lead to a substantial twist of one of the rings, thereby reducing the conjugation to the hexayne moiety.

Electrochemistry

For further exploration of the electron donor and acceptor properties of the chiral and achiral [AB]-type oligomers and their precursors, electrochemical investigations were carried out by cyclic voltammetry (CV) and rotating disk voltammetry (RDV) in CH_2Cl_2 with nBu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte. The redox potentials vs. Fc^+/Fc (ferricinium/ferrocene couple) are listed in Table 1 for the chiral derivatives and in Table 2 for the achiral derivatives.

Table 1. Cyclic voltammetry (CV; scan rate v = 0.1 V s^{-1}) and rotating disk voltammetry (RDV) data in CH_2Cl_2 (+ 0.1 M nBu$_4$NPF$_6$).[a]

	CV			RDV	
	$E°$ [V][b]	ΔE_p [mV][c]	E_p [V][d]	$E_{1/2}$ [V][e]	Slope [mV][f]
(*R*)-**19**			+0.84		
	–1.82	60			
			–2.05		
(*R*)-**13**			+0.74	+0.74 (2e$^-$)[g]	60
	–0.81	65		–0.81 (1e$^-$)	80
			–1.23	–1.13 (1e$^-$)	80
(*S*)-**24**			+0.36	+0.36 (2e$^-$)	60
(*S*)-**27**	+0.86	60		+0.85 (2e$^-$)	60
	–0.82	60		–0.81 (1e$^-$)	60
	–0.92	60		–0.91 (1e$^-$)	60
	–1.31	60		–1.27 (2e$^-$)	125

[a] All potentials are given vs. the Fc^+/Fc couple used as internal standard. [b] $E° = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [c] $\Delta E_p = E_{pa} - E_{pc}$. [d] E_p = irreversible peak potential. [e] $E_{1/2}$ = half-wave potential. [f] Logarithmic analysis of the wave obtained by plotting E vs. Log$[I/(I_{lim} - I)]$. [g] Further oxidations lead to electrode inhibition.

Table 2. Cyclic voltammetry (CV; scan rate v = 0.1 V s^{-1}) and rotating disk voltammetry (RDV) data in CH_2Cl_2 (+ 0.1 M nBu$_4$NPF$_6$).[a]

	CV			RDV	
	$E°$ [V][b]	ΔE_p [mV][c]	E_p [V][d]	$E_{1/2}$ [V][e]	Slope [mV][f]
8			+0.59[g]	0.59 (2e$^-$)	75
			–1.80	–1.77 (1e$^-$)	50
9			+0.57	+0.53 (2e$^-$)	70
			–1.80	–1.78 (1e$^-$)	60
37	+0.92	75		+0.93 (1e$^-$)	70
	+0.56	75		+0.57 (1e$^-$)	65
	–0.58	75		–0.57 (1e$^-$)	60
	–0.94	75		–0.95 (1e$^-$)	75
41	+0.91	60		+0.91 (1e$^-$)	60
	+0.56	60		+0.56 (1e$^-$)	60
	–0.58	60		–0.60 (1e$^-$)	60
	–0.93	60		–0.96 (1e$^-$)	70
			–2.25		
42	+0.91	60		+0.92 (2e$^-$)	60
	–0.44	60		–0.44 (1e$^-$)	60
	–0.59	60		–0.59 (1e$^-$)	60
	–0.99	70		–1.03 (2e$^-$)	70
43	+0.55			+0.57 (1e$^-$)[h]	80
	+0.44			+0.47 (2e$^-$)	70
	–0.04	60		–0.04 (1e$^-$)	60
	–1.08	70		–1.10 (2e$^-$)	70
	–1.27	75		–1.28 (2e$^-$)	70
36	+0.92	80		+0.94 (2e$^-$)	40
	–0.34	70		–0.37 (1e$^-$)	65
	–0.66	70		–0.69 (1e$^-$)	60
	–1.17	130		–1.22 (2e$^-$)	75

[a] All potentials are given vs. the Fc^+/Fc couple used as internal standard. [b] $E° = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [c] $\Delta E_p = E_{pa} - E_{pc}$. [d] E_p = irreversible peak potential. [e] $E_{1/2}$ = half-wave potential. [f] Logarithmic analysis of the wave obtained by plotting E vs. log$[I/(I_{lim} - I)]$. [g] Reversible electron transfer at scan rates > 2 V s^{-1}. [h] Further oxidations lead to electrode inhibition.

Chiral [AB]-Type Oligomers

Compound (*S*)-**24** exhibits an irreversible 2e$^-$ oxidation step (+0.36 V from CV) on the two DMA units. For (*S*)-**27**, the reversible 2e$^-$ oxidation at +0.86 V (CV) involves the two independent DMA moieties. Oxidation of the DMA units in (*S*)-**27** is rendered more difficult by the conjugation with the strong TCBD acceptors. In (*S*)-**27**, the reduction of the two TCBDs occurs in two successive reversible 1e$^-$ processes at –0.81 V and –0.91 V (RDV), respectively. The third reversible reduction involving 2e$^-$ [–1.27 V (RDV)] is unresolved. In general, the redox properties of the chiral TCBD dimer (*S*)-**27** are quite similar to those of its achiral analogue having a H substituent instead of the binaphthyl substituent.[3] The first reduction potential is shifted to a slightly more negative value for (*S*)-**27** (–0.82 V in CV vs. –0.69 V), probably due to the presence of the binaphthyl moiety which acts as an additional electron donating substituent in (*S*)-**27**.

Compound (*R*)-**19** shows one irreversible oxidation (+0.84 V from CV) centered on the 1,2-bis(1,3-dithiol-2-ylidene)ethane unit. In RDV, no potential could be determined. It should be noted that (*R*)-**19** was poorly soluble during the measurements and its CV was not well-defined.

For (*R*)-**13**, the oxidation also occurs on the extended TTF moiety in a single irreversible 2e⁻ transfer (+0.74 V). The parent TTF undergoes the oxidation steps at –0.08 V and +0.4 V under the same conditions.[45] Thus, oxidation of this moiety in (*R*)-**19** and (*R*)-**13** becomes more difficult by the conjugation with the dicyanovinyl acceptor.

The CV of (*R*)-**19** shows one reversible reduction on the dicyanovinyl unit at –1.82 V and another irreversible reduction at more negative potential (–2.05 V). For (*R*)-**13**, the reduction of the TCBD moiety occurs in two 1e⁻ steps at –0.81 V and –1.13 V (RDV), respectively, the second one being irreversible. In contrast to previous studies on TCBDs, the expected reversible 1e⁻ reduction of the dicyanovinyl unit is not observed, probably due to electrode inhibition or poor solubility of the reduced species.

For (*R*)-**13** with its additional TCBD acceptor, the first oxidation potential for the extended TTF unit (+0.74 V) is shifted cathodically by 100 mV, when compared to (*R*)-**19** (+0.84 V). This result clearly indicates the strongly reduced π-conjugation between the TCBD and the extended TTF units in (*R*)-**13**. ^{1}H NMR spectra show the presence of complex conformational equilibria for (*R*)-**13** (Supporting Information). Additionally, the first reduction of (*R*)-**13** in CV (–0.81 V) is shifted anodically as compared to (*R*)-**19** (–1.82 V), due to the presence of the additional electroactive TCBD acceptor.

Achiral [AB]-Type Oligomers

Hexaynes **8** (+0.59 V from CV) and **9** (+0.57 V from CV) show an irreversible 2e⁻ oxidation on the DHA and *N*,*N*-diisopropylanilino moieties, respectively. For **37** [+0.92 and +0.56 V (CV)] and **41** [+0.91 and +0.56 V (CV)], two well-defined, reversible 1e⁻ oxidations were observed. The potentials measured for **8/9** and **37/41**, respectively, are similar, as expected for derivatives with almost identical structures.

Tetrayne **42** undergoes a reversible 2e⁻ oxidation at +0.91 V (CV) involving the two independent diisopropylanilino redox centers. The oxidation of **43** occurs in three steps at –0.04 V (1e⁻ exchange), +0.44 V (2e⁻ exchange), and +0.55 V (1e⁻ exchange), respectively. The two last oxidations are not well resolved and lead to electrode inhibition during RDV. The first oxidation of **43** occurs at a very low potential of –0.04 V; for comparison, the first oxidation potential of unsubstituted TTF is –0.08 V vs. the Fc^+/Fc couple.[45] A similar first oxidation potential was also observed for **5** (see Scheme 1); in this case, it was supposed that the steric crowding results in a highly twisted structure and therefore extended π-conjugation is no longer possible.[24] ^{1}H NMR spectra of **43** also indicate complex conformational equilibria due to steric crowding. Probably, the conjugation between the TCBD acceptor and the extended TTF donor moiety in **43** is strongly reduced, thus shifting the first oxidation potential of the latter to lower values. Interestingly, a TCNE-TTF adduct with a very similar structure to one half of symmetric **43**, exhibits the first oxidation at a much higher potential of +0.38 V vs. –0.04 V for **43** (CV).[24] Thus, it is assumed that "dimeric" **43** is much more twisted than its "monomeric" analogue. It can be concluded, that there is no general trend for the redox behavior of this class of nonplanar chromophores and that each compound may behave in a particular way, depending on the equilibrium between its different conformers in solution.

The two DMA moieties in bisadduct **36** are oxidized in a single two-electron step at +0.92 V (CV). This value is in very good agreement with the oxidation potential observed for bisadduct **42** in CV (+0.91 V, see above). The peak shapes in cyclic voltammetry and the value of the peak potential difference (80 mV) indicate that the two DMA moieties in **36** are oxidized stepwise in two reversible one-electron transfers. The redox potentials of the two one-electron transfers are separated by about 60 mV.

Compounds **8** [–1.80 V (CV)] and **9** [–1.80 V (CV)] show irreversible 1e⁻ reductions on the 1,3,5,7,9,11-dodecahexayne moiety, which acts as a weak electron acceptor. For **37** [–0.58 and –0.94 V (CV)] and **41** [–0.58 and –0.93 V (CV)], two reversible 1e⁻ reductions located on the two dicyanovinyl moieties were observed. As already described above for their oxidation, the reduction potentials for compounds **8/9** and **37/41**, respectively, are nearly identical. The reduction of the TCBD units in **42** occurs in three steps, the first two reductions at –0.44 and –0.59 V, respectively, are reversible 1e⁻ transfers, whereas the third reduction step at –0.99 V (CV) involves a global 2e⁻ transfer. From the peak shape and the peak characteristics of this third reduction, it is clear that it results from the overlap of two reversible 1e⁻ transfers, of which the redox potentials are separated by only 50 mV, giving rise to an unresolved CV.[46,47] The reduction of **43** involves two reversible 2e⁻ transfers at –1.08 and –1.27 V (CV) occurring on the two TCBD moieties. From the peak shapes, each peak results from the overlap of two reversible 1e⁻ transfers occurring on the two quite independent TCBD redox centers. The lack of either electrostatic or π-conjugation interactions may be due to steric crowding in **43** resulting in a twisted structure (see above), in contrast to **42** for which a more planar structure is assumed. For **36**, the first two reductions [–0.34 and –0.66 V (CV)] seem to occur on the two dicyanovinyl moieties, which are conjugated through the butadiyne spacer. This explains the potential difference between the two dicyanovinyl groups. As the two remaining dicyanovinyl groups in the charged species (dianion) are most probably not planar, and therefore not in conjugation with each other, their reduction occurs at quite similar potentials giving rise to a unique reversible 2e⁻ step [–1.17 V (CV)]. From its peak shape and peak potential difference of 130 mV, it is clear that this step involves two 1e⁻ exchanges. The redox potentials of the two steps are separated by about 80 mV. In general, the redox properties of bisadduct **36** are quite similar to those of its extended analogue **42**.

For the extended TCBDs **37** and **41**, a substantially lowered electrochemical HOMO–LUMO gap of 1.14 V (from CV) is observed, as compared to a known TCBD derivative with only one triple bond (1.61 V from CV).[3,4] As shown

previously, this is a direct consequence of the reduction in the D-A conjugation by the longer 1,3,5,7,9-decapentayn-1-yl spacer in **37** and **41**, as compared to the ethynediyl spacer.[4,33,48]

UV/Vis and CD Spectroscopy

The UV/Vis absorption spectra of the chiral and achiral multivalent CT chromophores were recorded to gain further insight into their opto-electronic properties. The CD spectra were measured to investigate whether conformational preferences and a sense of chirality were induced in the dendralene-type backbones of the chiral [AB]-type oligomers.

Chiral [AB]-Type Oligomers

The intense band at 230 nm (5.40 eV, 66800 $M^{-1}cm^{-1}$, Figure 4) in the UV/Vis spectrum of (*R*)-**13** in MeCN is assigned to the naphthyl π→π* transition by comparison to the UV/Vis and CD spectra of its precursor (*R*)-**44** (Supporting Information) and to the published spectra of a closely related derivative.[49] Corresponding to this band there is an intense Cotton effect at 236 nm (5.26 eV, $\Delta\varepsilon$ = –61 $M^{-1}cm^{-1}$) in the CD spectrum of (*R*)-**13** (MeCN, Figure 4). In addition, the UV/Vis spectrum of (*R*)-**13** shows a weak CT absorption at 478 nm (2.60 eV). In the same region, the CD spectrum shows a bisignate band at 433 nm (2.87 eV, $\Delta\varepsilon$ = –6 $M^{-1}cm^{-1}$) and 527 nm (2.36 eV, $\Delta\varepsilon$ = +3 $M^{-1}cm^{-1}$). This points at a weak chiral induction from the binaphthyl moiety into the [AB]-type oligomer. VT-CD spectroscopy showed no significant change in the spectrum over the range from –10 to 70 °C (Supporting Information). The intensity of the weak bisignate band corresponding to the CT absorption of the dendralene-type backbone did not change upon lowering the temperature. The weak chiral induction presumably originates from the lack of strong conformational preferences in (*R*)-**13**. A single stable chiral conformer should exhibit a higher intensity of the Cotton effects in the region of the CT absorption, as was recently observed in conformationally highly preorganized optically active allenes conjugated to donor-substituted TCBD chromophores [e.g. (*M*)-**12**, Figure 2].[26,27]

The UV/Vis and CD spectra of (*S*)-**23** and (*S*)-**24** can be found in the Supporting Information. Compound (*S*)-**23** shows a bisignate band between 413 nm (3.01 eV) and 466 nm (2.67 eV, $\Delta\varepsilon$ = +3 and –6 $M^{-1}cm^{-1}$, respectively), which is associated with the broad CT band at 425 nm (2.92 eV, ε = 40000 $M^{-1}cm^{-1}$) in the UV/Vis spectrum.

The UV/Vis spectrum of (*S*)-**27** shows an intense band at 226 nm (5.50 eV, ε = 77300 $M^{-1}cm^{-1}$, Figure 5). The corresponding Cotton effect in the CD spectrum is located at 232 nm (5.35 eV, $\Delta\varepsilon$ = +87 $M^{-1}cm^{-1}$). These bands can be assigned to the binaphthyl moiety. Two CT bands are observed at 384 (3.24 eV, ε = 37900 $M^{-1}cm^{-1}$) and 532 nm (2.34 eV, ε = 18500 $M^{-1}cm^{-1}$) in the UV/Vis spectrum. The CT nature of these bands was proven by acidification with trifluoroacetic acid (TFA), followed by neutralization with NEt_3 (Supporting Information). In the CD spectrum, a weak bisignate band between 350 nm (3.55 eV) and 398 nm (3.12 eV, $\Delta\varepsilon$ = +5 and –5 $M^{-1}cm^{-1}$, respectively) is associated with the CT absorption at 384 nm. Similar to (*R*)-**13** and (*S*)-**23**, this points at a weak chiral induction from the chiral binaphthyl into the two TCBD moieties. The intensities of the induced Cotton effects in (*R*)-**13**, (*S*)-**23**, and (*S*)-**27** ($\Delta\varepsilon$ from 3 to 6 $M^{-1}cm^{-1}$) are weaker than those in the spectra of chiral allenic push-pull conjugates [$\Delta\varepsilon$ from 12 to 30 $M^{-1}cm^{-1}$ for (*M*)-**12**].[26,27] This can be explained by a very low conformational stability in the binaphthyl system. It can be concluded that the 1,3-diethynylallene moiety is superior to the binaphthyl moiety for chiral induction into donor-substituted TCBDs.

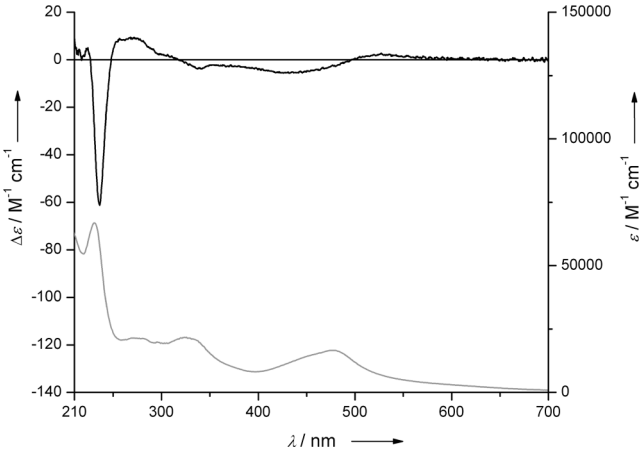


Figure 4. CD spectrum (top, black line) and UV/Vis spectrum (bottom, gray line) of (*R*)-**13** in MeCN at 298 K.

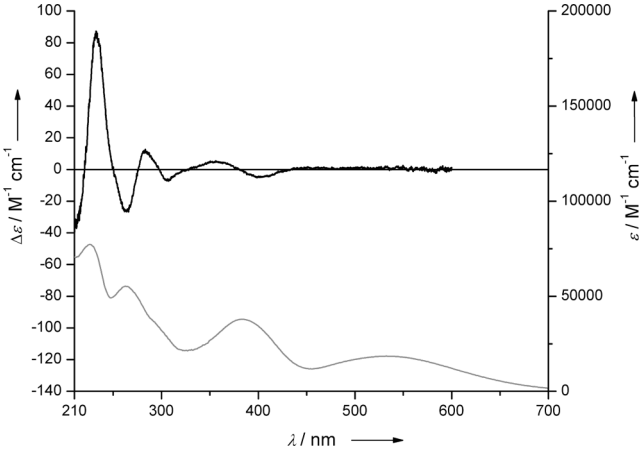


Figure 5. CD spectrum (top, black line) and UV/Vis spectrum (bottom, gray line) of (*S*)-**27** in MeCN at 298 K.

Achiral [AB]-Type Oligomers

The absorption spectra for hexaynes **8** and **9** in CH_2Cl_2 at 298 K are shown in Figure 6. As previously observed with symmetric end-capped hexaynes,[43,50] the spectra show well-resolved vibronic structures in the lower energy region

from 350 to 470 nm (3.55 to 2.64 eV). The bands in the higher-energy region from 280 to 350 nm (4.44 to 3.55 eV) are not well resolved in the case of anilino-substituted hexaynes **8** and **9**. The presence of the strong DHA and *N*,*N*-diisopropylanilino donors significantly changes the absorption spectra of **8** and **9** as compared to phenyl- or *p*-anisyl-substituted hexaynes reported by Tykwinski et al.[43] For **8** and **9**, the most intense absorptions are observed at 471 (2.64 eV, ε = 57700 $M^{-1}cm^{-1}$) and 440 nm (2.82 eV, ε = 56000 $M^{-1}cm^{-1}$), respectively, whereas the lowest energy absorptions for the two hexaynes are found at 517 (2.40 eV, ε = 26700 $M^{-1}cm^{-1}$) and 515 nm (2.41 eV, ε = 24100 $M^{-1}cm^{-1}$), respectively. The corresponding values measured in THF for the *p*-anisyl-substituted hexayne are 351 (3.54 eV, ε = 164000 $M^{-1}cm^{-1}$) and 476 nm (2.61 eV, ε = 13300 $M^{-1}cm^{-1}$). This is in agreement with the finding by Tykwinski et al. that increasing the donor-strength results in bathochromic shifts for absorptions in both regions.[43]

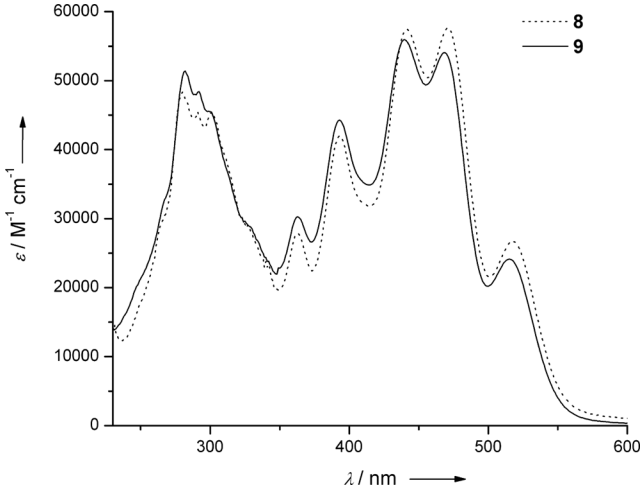


Figure 6. UV/Vis spectra of hexaynes **8** and **9** in CH_2Cl_2 at 298 K.

The molar absorptivities of **8** and **9** in the higher energy region [280 to 350 nm (4.44 to 3.55 eV, in CH_2Cl_2): 40000 to 50000 $M^{-1}cm^{-1}$] are much lower than the ones reported by Tykwinski (155000 to 200000 $M^{-1}cm^{-1}$ in THF) and Hirsch (164000 to 194000 $M^{-1}cm^{-1}$ in CH_2Cl_2).[43,50] In addition, the reported hexaynes show a large decrease in intensity when going to the lower energy region of the spectrum, whereas **8** and **9** show similar intensities in both regions. This indicates a large effect of the structure of the end-capping groups on the oscillator strength for extended oligoynes. The intensity of the absorptions between 350 and 470 nm was considerably lowered upon acidification of **8** with TFA. The bands were fully recovered after neutralization with NEt_3, thus revealing their CT character.

The UV/Vis spectra of extended TCBD **37**, and multivalent CT chromophores **38**, **39**, and **40** were measured in CH_2Cl_2 at 298 K (Figure 7). The D-A substituted chromophores display intense, broad CT bands with absorption maxima λ_{max} between 458 nm (2.71 eV, **40**) and 639 nm (1.94 eV, **37**). Compound **37** exhibits an additional CT band, which is significantly shifted to lower energies (λ_{max} = 639 nm, 1.94 eV), when compared to **38** (λ_{max} = 460 nm, 2.70 eV), **39** (λ_{max} = 484 nm, 2.57 eV), and **40** (λ_{max} = 458 nm, 2.71 eV). This is in agreement with the results from electrochemistry and clearly reflects the weaker D-A coupling in **37** caused by the additional 1,3,5,7,9-decapentayn-1,10-diyl spacer (see above). The UV/Vis spectra of **7**, **36**, **41**, **42**, and **43** are very similar to those of their DHA-substituted analogues (Supporting Information).

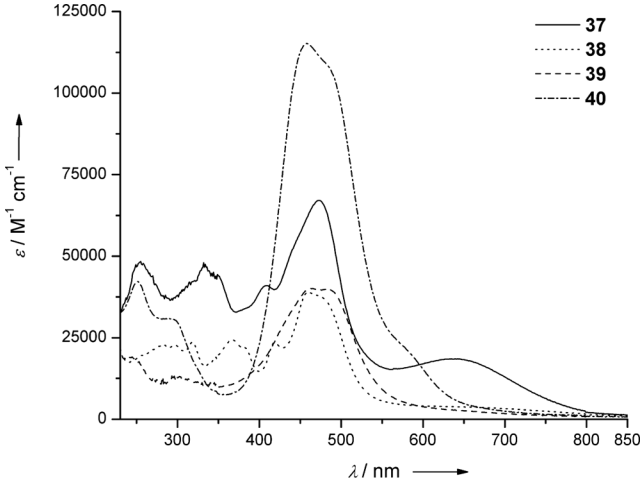


Figure 7. UV/Vis spectra of **37**, **38**, **39**, and **40** in CH_2Cl_2 at 298 K.

Nonlinear Optical Properties of TCBD 41

The third-order optical nonlinearity of the D-A-substituted TCBD **41** was determined by measuring the third-order susceptibility of CH_2Cl_2 solutions with varying molecular concentrations, which gave the rotational average of the third-order polarizability γ_{rot}.[51] The γ-values were determined by degenerate four-wave mixing (DFWM) at a wavelength of 1.5 μm and fused silica with $\chi^{(3)}$ = 1.9×10^{-22} m^2V^{-2} as a reference. The extended TCBD **41** exhibits an extraordinarily large γ_{rot} value of $(6 \pm 2) \times 10^{-47}$ m^5V^{-2}. For comparison, DDMEBT currently used in non-linear optics devices, displays under the same conditions a γ_{rot} value of $(1.2 \pm 0.2) \times 10^{-47}$ m^5V^{-2}.[3]

Conclusions

We prepared the optically active [AB]-type oligomers (*R*)-**13**, (*S*)-**23**, and (*S*)-**27** by TTF and TCNE additions to alkyne-substituted 1,1′-binaphthalene derivatives. CD spectroscopy revealed chiral induction from the axially chiral binaphthyl moieties into the dendralene-type backbone of (*R*)-**13** and the TCBD moieties of (*S*)-**23** and (*S*)-**27**. However, the large conformational heterogeneity of these compounds is adverse to high chiral induction, and the induced Cotton effects are of low intensity. Introduction of sterically more demanding substituents in the 2,2′-position of the binaphthyl moieties actually may lead to stronger chiral induction in future systems.

As a true highlight, we prepared the A–D–A–D chromophore **7** as a single product in 58% yield by a remarkable one-pot, eight-step, five-component cascade reaction starting from mono-DMA-, mono-4-cyanophenyl-substituted tetrayne **6**. This oligoyne is perfectly tuned for the strictly electronically controlled domino transformation. In previous work, electronically less perfectly tuned phenyl-substituted tetrayne **2** only gave a 21% yield in the same conversion.[24]

The symmetric 1,3,5,7,9,11-dodecahexaynes **8** and **9** were prepared in good yield by oxidative Hay coupling. Hexaynes **8** and **9** were successfully used to construct the new extended [AB]-type oligomers **39**, **40**, and **43** by successive TCNE/TTF additions. The intramolecular CT interactions in these new D-A chromophores were analyzed by electrochemistry and by UV/Vis spectroscopy, revealing the impact of strong steric overcrowding on π-electron conjugation between donor and acceptor moieties. The extended TCBDs **37** and **41** with low optical and electrochemical HOMO–LUMO gaps are interesting candidates for NLO chromophores. Thus, the third-order optical nonlinearity of **41** was measured by DFWM and an extraordinarily large γ_{rot} value of $(6 \pm 2) \times 10^{-47}$ m^5 V^{-2} was found.[33,52] This result may provide new directions for the design of future NLO chromophores.

Experimental Section

Materials and General Methods: Reagents and solvents were purchased at reagent grade from GFS Chemicals (TMSA), Acros, ABCR, Aldrich, and Fluka and used as received. THF was freshly distilled from Na/benzophenone, toluene from Na and CH_2Cl_2 from CaH_2 under N_2 atmosphere. For all aqueous solutions, deionized water was used. Hay catalyst refers to a freshly prepared solution of CuCl (65 mg, 0.66 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA; 80 mg, 0.69 mmol) in CH_2Cl_2 (5 mL) or to a freshly prepared solution of CuCl (400 mg, 4.0 mmol) and TMEDA (464 mg, 4.0 mmol) in acetone (100 mL). All reactions, except Hay couplings, were performed under an inert atmosphere by applying a positive pressure of argon. Drying was performed in vacuo at 10^{-2} Torr. Solvents for flash chromatography (FC), medium pressure liquid chromatography (MPLC), plug filtrations, and extractions were of technical quality and distilled before use. The chromatographic separations were carried out on SiO_2 60 (particle size 0.040–0.063 mm, 230–400 mesh; Silicycle). FC was carried out at an overpressure of 0.1–0.6 bar. MPLC was performed with a Büchi Sepacore system consisting of a Büchi Pump manager C-615, a Büchi Pump Module C-601, and a Büchi Fraction collector C-660. Thin-layer chromatography (TLC) was conducted on SiO_2-layered glass plates (60 F_{254}, Merck); visualization with UV light (254 or 366 nm). Compounds 4,4′-(octa-1,3,5,7-tetrayne-1,8-diyl)-bis(*N*,*N*-dimethylaniline) (**1**),[24] (*R*)-3-ethynyl-2,2′-dimethoxy-1,1′-binaphthalene [(*R*)-**15**],[31] (*S*)-3,3′-diiodo-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl [(*S*)-**21**],[53] 4-(buta-1,3-diyn-1-yl)-*N*,*N*-dimethylaniline (**22**),[4] (*S*)-3,3′-diiodo-2,2′-diethoxy-1,1′-binaphthyl [(*S*)-**25**],[35] 4-ethynyl-*N*,*N*-dimethylaniline (**26**),[36] 4-ethynyl-*N*,*N*-dihexylaniline (**30**),[37] 4-[4-(trimethylsilyl)buta-1,3-diyn-1-yl]benzonitrile (**34**),[40] and 4-[4-(trimethylsilyl)buta-1,3-diyn-1-yl]-*N*,*N*-dimethylaniline (**35**)[4] were prepared according to literature procedures. Liquid chromatography/mass spectrometry (LC/MS) was performed on an Ultimate 3000 series LC instrument combined with an MSQ Plus mass spectrometer from Dionex, using a Zorbax Eclipse Plus C18 column (30 × 3 mm; 3.5 μm pore size) from Agilent or a Reprospher C18-Aqua column (30 × 3 mm; 3 μm pore size) from Dr. Maisch. Melting points (M.p.) were measured on a Büchi B-540 melting-point apparatus in open capillaries and are uncorrected. "Decomp." refers to decomposition. ^{1}H NMR and ^{13}C NMR spectra were measured on Varian Mercury 300, Bruker ARX 300, Bruker DRX400, Bruker AV400, or Bruker DRX 500 instruments at 298 K, unless otherwise stated. Chemical shifts are reported in ppm relative to the signal of tetramethylsilane. Residual solvent signals in the ^{1}H and ^{13}C NMR spectra were used as an internal reference. Coupling constants (*J*) are given in Hz. The apparent resonance multiplicity is described as s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplets), t (triplet), q (quartet), sep (septet), and m (multiplet). Infrared spectra (IR) were recorded neat on a Varian 800 FT-IR instrument. Absorption bands are reported in cm^{-1}. UV/Vis spectra were recorded on a Varian Cary-5 spectrophotometer. The spectra were measured in CH_2Cl_2 or MeCN in a quartz cuvette (1 cm) at 298 K. The absorption wavelengths are reported in nm with the extinction coefficient ε (M^{-1} cm^{-1}) in brackets; shoulders are indicated as sh. Optical rotation values were measured on a Perkin–Elmer 241 Polarimeter. Circular dichroism spectra were measured with a JASCO J-715 spectropolarimeter. High-resolution- (HR) EI-MS spectra were measured on a Waters Micromass AutoSpec-Ultima spectrometer, HR-ESI-TOF-MS spectra on a Bruker maXis ESI-Q-TOF spectrometer and HR-FT-ICR-MALDI-MS and ESI-MS spectra on a Varian IonSpec Fourier Transform (FT) ICR instrument with (3-hydroxypyridine-2-carboxylic acid) (3-HPA) or ({(2*E*)-3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidene}malononitrile) (DCTB) as matrix. The most important signals are reported in *m*/*z* units with M^+ as the molecular ion. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH Zürich, with a LECO CHN/900 instrument. The nomenclature was generated with ACD Name 9 by Advanced Chemistry Development Inc.

Electrochemistry: Electrochemical measurements were carried out at 20 °C in CH_2Cl_2 containing 0.1 M nBu$_4$NPF$_6$ in a classical three-electrode cell. CH_2Cl_2 was purchased in spectroscopic grade from Merck, dried with molecular sieves (4 Å), and stored under Ar prior to use. nBu$_4$NPF$_6$ was purchased in electrochemical grade from Fluka and used as received. The working electrode was a glassy carbon disk electrode (3 mm in diameter) used either motionless for cyclic voltammetry (CV; 0.1 to 10 V s^{-1}) or as rotating-disk electrode for rotating disk voltammetry (RDV). The auxiliary electrode was a Pt wire, and the reference electrode was either an aqueous Ag/AgCl electrode or a platinum wire used as a pseudo-reference electrode. All potentials are referenced to the ferricinium/ferrocene (Fc^+/Fc) couple, used as an internal standard, and are uncorrected from ohmic drop. The cell was connected to an Autolab PGSTAT20 potentiostat (Eco Chemie BV, Utrecht, The Netherlands) driven by a GPSE software running on a personal computer.

X-ray Analysis: The structure was solved by direct methods (SIR-97)[54] and refined by full-matrix least-squares analysis (SHELXL-97).[55] All non H-atoms were refined anisotropically; H-atoms were refined isotropically.

X-ray Crystal Structure of 9: Crystal data at 203 K for $C_{36}H_{36}N_2$, M_r = 496.70, triclinic, space group $P\bar{1}$, D_x = 1.129 g cm^{-3}, Z = 2, a = 7.5937(3), b = 10.9722(5), c = 18.8897(10) Å, α = 73.854(2)°, β = 79.346(2)°, γ = 77.172(3)°, V = 1461.28(12) Å^3. Bruker-Nonius

Kappa-CCD diffractometer, Mo-K_α radiation, λ = 0.7107 Å, μ = 0.065 mm^{-1}. A red crystal of **9** (linear dimensions ca. 0.2 × 0.15 × 0.02 mm) was obtained by slow evaporation of a solution of **9** in CH_2Cl_2 at 25 °C. Numbers of measured and unique reflections are 10106 and 6453, respectively (R_{int} = 0.054). Final $R(F)$ = 0.0656, w$R(F^2)$ = 0.1622 for 487 parameters and 3704 reflections with $I > 2\sigma(I)$ and $2.425 < \theta < 27.485°$ (corresponding R values based on all 6453 reflections are 0.1269 and 0.2033, respectively).

CCDC-758914 contains the supplementary crystallographic data (excluding structure factors) for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223)-336-033; E-mail: deposit@ccdc.cam.ac.uk], or via www.ccdc.cam.ac.uk/data_request/cif.

(*R*)-5-(2,2′-Dimethoxy-1,1′-binaphthalen-3-yl)penta-2,4-diyn-1-ol [(*R*)-16] and (*R*,*R*)-3,3′-(Buta-1,3-diyne-1,4-diyl)bis(2,2′-dimethoxy-1,1′-binaphthalene) [(*R*,*R*)-17]: To a solution of (*R*)-**15** (133 mg, 0.393 mmol) and prop-2-yn-1-ol (0.23 mL, 223 mg, 3.97 mmol) in CH_2Cl_2 (35 mL), a solution of Hay catalyst in CH_2Cl_2 (5 mL) was added and the resulting solution stirred exposed to air for 18 h at 25 °C. Evaporation of the solvent in vacuo and subsequent purification by FC (heptane/AcOEt, 9:1, heptane/AcOEt, 8:2, heptane/AcOEt, 7:3) gave (*R*,*R*)-**17** as a light brown solid (24 mg, 18%) and (*R*)-**16** as a light brown solid (78 mg, 51%).

(*R*)-16: R_f = 0.0 (SiO_2, heptane/AcOEt, 8:2); m.p. 93–96 °C; $[\alpha]_D^{20}$ = +120 (c = 0.1, $CHCl_3$). ^{1}H NMR (300 MHz, CD_3OD): δ = 3.50 (s, 3 H), 3.72 (s, 3 H), 4.22 (s, 2 H), 4.33 (s, 1 H), 6.93–6.98 (m, 2 H), 7.12–7.37 (m, 4 H), 7.50 (d, J = 9.1 Hz, 1 H), 7.80–7.86 (m, 2 H), 8.01 (d, J = 9.0 Hz, 1 H), 8.14 (s, 1 H) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 50.56, 50.84, 56.25, 61.05, 69.06, 69.57, 75.29, 77.62, 78.44, 83.09, 113.99, 116.35, 118.64, 124.23, 125.34, 126.15, 127.22, 128.27, 128.73, 130.05, 130.80, 131.28, 134.66, 135.28, 136.00, 155.77, 156.79 ppm. IR (neat): $\tilde{\nu}$ = 3270, 2933, 2837, 1619, 1592, 1509, 1495, 1456, 1407, 1355, 1335, 1267, 1248, 1220, 1147, 1092, 1016, 913, 807, 748 cm^{-1}. HR-EI-MS m/z (%): calcd. for $C_{27}H_{20}O_3^+$: 392.1407; found 392.1406 (100, $[M]^+$).

(*R*,*R*)-17: R_f = 0.1 (SiO_2, heptane/AcOEt, 8:2); m.p. 111–113 °C; $[\alpha]_D^{20}$ = +162 (c = 0.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.63 (s, 6 H), 3.80 (s, 6 H), 7.08–7.12 (m, 4 H), 7.22–7.42 (m, 8 H), 7.46 (d, J = 9.1 Hz, 2 H), 7.83–7.89 (m, 4 H), 8.01 (d, J = 9.0 Hz, 2 H), 8.22 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.52, 61.27, 78.10, 79.38, 113.29, 116.00, 118.15, 123.51, 124.91, 125.23, 125.46, 125.58, 126.58, 127.39, 127.75, 127.81, 128.84, 129.78, 130.08, 133.75, 134.22, 135.28, 154.64, 155.97 ppm. IR (neat): $\tilde{\nu}$ = 3055, 2918, 2848, 2359, 2342, 1734, 1620, 1592, 1508, 1456, 1404, 1356, 1333, 1264, 1246, 1147, 1078, 1016, 806, 746 cm^{-1}. HR-FT-MALDI-MS (3-HPA) m/z (%): calcd. for $C_{48}H_{34}O_4^+$: 674.2452; found 674.2463 (82, $[M]^+$).

(*R*)-[5-(2,2′-Dimethoxy-1,1′-binaphthalen-3-yl)penta-2,4-diyn-1-ylidene]malononitrile [(*R*)-18]: Dess–Martin periodinane (211 mg, 0.497 mmol, 15% solution in CH_2Cl_2) was added to a solution of (*R*)-**16** (78 mg, 0.199 mmol) in CH_2Cl_2 (30 mL). The resulting solution was stirred for 1 h at 25 °C, filtered through a plug (SiO_2; CH_2Cl_2), and concentrated in vacuo to ca. 50% of its original volume. Malononitrile (27 mg, 0.402 mmol) and Al_2O_3 (122 mg, 1.193 mmol) were added, and the solution was stirred for 1 h at 50 °C. Purification by FC (heptane/AcOEt, 8:2, heptane/AcOEt, 7:3, heptane/AcOEt, 1:1) afforded (*R*)-**18** as a light brown oil (28 mg, 32%). R_f = 0.2 (SiO_2, heptane/AcOEt, 8:2); $[\alpha]_D^{20}$ = +114 (c = 0.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.55 (s, 3 H), 3.81 (s, 3 H), 7.05–7.14 (m, 2 H), 7.23–7.37 (m, 4 H), 7.41–7.48 (m, 2 H), 7.86–7.90 (m, 2 H), 8.03 (d, J = 9.1 Hz, 1 H), 8.28 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.36, 61.39, 75.46, 92.80, 96.19, 98.58, 110.97, 112.10, 113.17, 114.07, 117.43, 123.66, 124.66, 125.65, 125.72, 125.85, 126.81, 127.86, 127.97, 128.24, 128.62, 128.87, 129.92, 130.17, 133.63, 135.37, 136.77, 140.04, 154.73, 155.93 ppm. IR (neat): $\tilde{\nu}$ = 2960, 2923, 2851, 2179, 2133, 1691, 1618, 1588, 1556, 1508, 1458, 1408, 1357, 1334, 1260, 1248, 1148, 1076, 1004, 892, 798, 748 cm^{-1}. HR-EI-MS m/z (%): calcd. for $C_{30}H_{18}N_2O_2^+$: 438.1363; found 438.1361 (100, $[M]^+$).

[2+2] Cycloaddition of TTF with Alkynes. General Method: A mixture of the alkyne (0.06 mmol, 1 equiv.) and TTF (2–5 equiv. per reacting C≡C bond) in CH_2Cl_2/MeCN, 1:1 (10 mL) was stirred at 50 °C for the indicated time. The solvent was evaporated in vacuo and the residue subjected to FC.

(*R*)-[5-(2,2′-Dimethoxy-1,1′-binaphthalen-3-yl)-2,3-(di-1,3-dithiol-2-ylidene)-4-pentyn-1-ylidene]malononitrile [(*R*)-19]: The title compound was prepared from (*R*)-**18** (25 mg, 0.057 mmol), according to the general method. The mixture was stirred for 13 h at 50 °C and purified by FC (CH_2Cl_2) to give (*R*)-**19** as a dark brown solid (12 mg, 33%). R_f = 0.3 (SiO_2, CH_2Cl_2); m.p. > 175 °C (decomp.); $[\alpha]_D^{20}$ = +183 (c = 0.01, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.65 (s, 3 H), 3.78 (s, 3 H), 6.47 (d, J = 6.6 Hz, 1 H), 6.58 (d, J = 6.6 Hz, 1 H), 6.90–6.94 (m, 2 H), 7.05 (d, J = 8.4 Hz, 1 H), 7.11 (d, J = 8.5 Hz, 1 H), 7.18–7.24 (m, 2 H), 7.29–7.38 (m, 3 H), 7.45 (d, J = 9.1 Hz, 1 H), 7.81 (d, J = 8.2 Hz, 1 H), 7.86 (d, J = 8.1 Hz, 1 H), 7.99 (d, J = 9.1 Hz, 1 H), 8.10 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 56.48, 61.31, 70.63, 90.41, 94.84, 97.82, 113.48, 113.64, 116.88, 117.20, 117.54, 118.76, 119.66, 121.32, 123.30, 123.59, 124.09, 125.15, 125.19, 125.58, 125.63, 126.60, 126.80, 127.70, 127.88, 129.03, 129.71, 130.43, 133.30, 133.87, 134.02, 147.18, 154.8, 155.13, 157.05, 170.53 ppm. IR (neat): $\tilde{\nu}$ = 3062, 2960, 2932, 2836, 2358, 2340, 2207, 1726, 1620, 1592, 1535, 1516, 1494, 1428, 1408, 1331, 1310, 1261, 1247, 1218, 1147, 1072, 1005, 906, 802 cm^{-1}. HR-FT-MALDI-MS (3-HPA) m/z (%): calcd. for $C_{36}H_{22}N_2O_2S_4Na^+$: 665.0456; found 665.0456 (100, $[M + Na]^+$).

[2+2] Cycloaddition of TCNE with Alkynes. General Method: A mixture of the alkyne (1 equiv.) and the indicated amount of TCNE (0.7–12.0 equiv. per reacting C≡C bond) in CH_2Cl_2 was stirred at 25 °C for the indicated time. The solvents were evaporated in vacuo and the residue subjected to FC.

(*R*)-3-(Dicyanomethylene)-2-(2,2′-dimethoxy-1,1′-binaphthalen-3-yl)-4,5-(di-1,3-dithiol-2-ylidene)-1,6-heptadiene-1,1,7,7-tetracarbonitrile [(*R*)-13]: The title compound was prepared from (*R*)-**19** (10 mg, 0.016 mmol) and TCNE (24 mg, 0.19 mmol) in CH_2Cl_2 (20 mL), according to the general method. The mixture was stirred for 24 h and purified by FC (CH_2Cl_2, CH_2Cl_2/AcOEt, 95:5, CH_2Cl_2/AcOEt, 9:1) to give (*R*)-**13** as a brown solid (6 mg, 50%). R_f = 0.5 (SiO_2, CH_2Cl_2/AcOEt, 99:1); m.p. 225–228 °C; $[\alpha]_D^{20}$ = +135 (c = 0.01, CH_2Cl_2). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 3.11–3.31 (m, 3 H), 3.81–3.93 (m, 3 H), 6.89–7.50 (m, 10 H), 7.87–8.09 (m, 4 H) (20 out of 22) ppm.[56] ^{13}C NMR (75 MHz, CD_2Cl_2): not available due to low solubility. IR (neat): $\tilde{\nu}$ = 3072, 2921, 2851, 2342, 2360, 2209, 1734, 1618, 1587, 1540, 1416, 1353, 1310, 1247, 1149, 1021, 948, 887, 810, 743 cm^{-1}. UV/Vis (MeCN): λ_{max} (ε) = 230 (66800), 324 (21800), 478 nm (16600 M^{-1} cm^{-1}). CD (MeCN): λ_{max} ($\Delta\varepsilon$) = 224 (+5), 236 (–61), 268 (+10), 337 (–4), 433 (–6), 527 nm (+3 M^{-1} cm^{-1}). HR-FT-MALDI-MS (3-HPA) m/z (%): calcd. for $C_{42}H_{22}N_6O_2S_4Na^+$: 793.0579; found 793.0565 (100, $[M + Na]^+$).

(*S*)-2,2′-{[2,2′-Bis(methoxymethoxy)-1,1′-binaphthalene-3,3′-diyl]-bis(2,1-ethynediyl)}bis{3-[4-(dimethylamino)phenyl]-1,3-butadiene-

1,1,4,4-tetracarbonitrile} [(*S*)-23]: To a solution of (*S*)-**20** (27 mg, 0.038 mmol) in MeCN/CH_2Cl_2, 3:1 (20 mL), TCNE (25 mg, 0.191 mmol) and TTF (40 mg, 0.193 mmol) were added. The mixture was stirred for 18 h at 50 °C. Evaporation of the solvent and subsequent FC (CH_2Cl_2, CH_2Cl_2/AcOEt, 95:5, CH_2Cl_2/AcOEt, 8:2) afforded (*S*)-**23** as a black solid (11 mg, 29%). R_f = 0.7 (SiO_2, CH_2Cl_2/AcOEt, 95:5); $[\alpha]_D^{20}$ = +15 (*c* = 0.01, CH_2Cl_2). ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): δ = 2.20 (s, 6 H), 3.07 (s, 12 H), 4.62 (d, *J* = 6.4 Hz, 2 H), 4.83 (d, *J* = 6.3 Hz, 2 H), 6.67 (d, *J* = 9.4 Hz, 4 H), 7.09 (d, *J* = 8.5 Hz, 2 H), 7.32–7.48 (m, 4 H), 7.73 (d, *J* = 9.4 Hz, 4 H), 7.86 (d, *J* = 8.0 Hz, 2 H), 8.34 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $C_2D_2Cl_4$): δ = 30.18, 40.70, 56.70, 89.84, 94.30, 110.87, 112.07, 112.73, 113.84, 114.07, 114.95, 115.41, 117.27, 126.41, 127.10, 127.21, 130.34, 130.36, 130.46, 132.94, 136.15, 139.64, 139.66, 151.23, 153.08, 155.07, 159.95 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 233 (54100), 291 (25300), 425 nm (40000 $M^{-1}cm^{-1}$). CD (CH_2Cl_2): λ_{max} ($\Delta\varepsilon$) = 237 (+26), 282 (–10), 367 (–7), 413 (+3), 466 nm (–6 $M^{-1}cm^{-1}$). HR-FT-MALDI-MS (3-HPA) *m*/*z* (%): calcd. for $C_{60}H_{40}N_{10}O_4Na^+$: 987.3126; found 987.3124 (70, [M + Na]$^+$).

(*S*)-2,2′-(2,2′-Diethoxy-1,1′-binaphthalene-3,3′-diyl)bis{3-[4-(dimethylamino)phenyl]-1,3-butadiene-1,1,4,4-tetracarbonitrile} [(*S*)-27]: The title compound was prepared from (*S*)-**24** (73 mg, 0.116 mmol) and TCNE (41 mg, 0.32 mmol) in CH_2Cl_2 (5 mL), according to the general method. The mixture was stirred for 18 h and purified by FC (heptane/CH_2Cl_2, 1:1, heptane/CH_2Cl_2, 3:7, heptane/CH_2Cl_2, 1:9, CH_2Cl_2, CH_2Cl_2/AcOEt, 8:2) to give (*S*)-**27** as a red solid (72 mg, 70%). R_f = 0.1 (SiO_2, CH_2Cl_2); m.p. 202–205 °C; $[\alpha]_D^{20}$ = +1467 (*c* = 0.0033, mg mL^{-1}, MeCN).[57] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.60 (t, *J* = 7.0 Hz, 6 H), 3.14–3.20 (m, 14 H), 3.32–3.37 (m, 2 H), 6.73 (d, *J* = 9.3 Hz, 4 H), 7.18 (d, *J* = 8.3 Hz, 2 H), 7.40–7.52 (m, 4 H), 7.75 (d, *J* = 9.3 Hz, 4 H), 7.97 (d, *J* = 8.4 Hz, 2 H), 8.21 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.43, 40.20, 69.60, 92.44, 111.15, 111.80, 112.22, 113.64, 114.58, 119.32, 122.32, 125.60, 126.30, 127.18, 128.60, 129.57, 130.27, 132.89, 133.00, 134.19, 136.52, 152.11, 154.02, 164.97, 167.06 ppm. IR (neat): $\tilde{\nu}$ = 3067, 2981, 2919, 2215, 1601, 1539, 1486, 1438, 1377, 1341, 1291, 1206, 1170, 1125, 1064, 1018, 943, 898, 824, 750 cm^{-1}. UV/Vis (MeCN): λ_{max} (ε) = 201 (73900), 226 (77300), 262 (55300), 384 (37900), 532 nm (18500 $M^{-1}cm^{-1}$). CD (MeCN): λ_{max} ($\Delta\varepsilon$) = 207 (–42), 232 (+87), 264 (–27), 283 (+13), 307 (–7), 350 (+5), 398 nm (–5 $M^{-1}cm^{-1}$). HR-FT-MALDI-MS (3-HPA) *m*/*z* (%): calcd. for $C_{56}H_{41}N_{10}O_2^+$: 885.3409; found 885.3402 (100, [M + H]$^+$).

4-[6-(Trimethylsilyl)hexa-1,3,5-triyn-1-yl]-*N*,*N*-dihexylaniline (28) and 4,4′-(Octa-1,3,5,7-tetrayne-1,8-diyl)bis(*N*,*N*-dihexylaniline) (31): K_2CO_3 (1409 mg, 10.19 mmol) was added to a solution of **29** (664 mg, 1.74 mmol) in MeOH/THF, 1:1 (100 mL). The mixture was stirred for 2 h at 25 °C, and CH_2Cl_2 (80 mL) was added. The organic phase was washed with H_2O (2 × 50 mL), dried ($MgSO_4$), and evaporated to yield deprotected **29** as a brown oil. The oil was dissolved in acetone (20 mL), and TMSA (2.51 mL, 1.74 g, 17.74 mmol) and Hay catalyst in acetone (100 mL) were added. The resulting mixture was stirred exposed to air for 3 h at 25 °C. The mixture was filtered through a plug (SiO_2; acetone), the solvent evaporated, the residue preadsorbed on SiO_2, and purified by FC (heptane, heptane/CH_2Cl_2, 98:2, heptane/CH_2Cl_2, 95:5) to afford **28** (355 mg, 50%) as a dark brown solid and **31** (81 mg, 15%) as a red-brown oil.

28: R_f = 0.3 (SiO_2, heptane/CH_2Cl_2, 9:1); m.p. > 40 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.21 (s, 9 H), 0.88–0.92 (m, 6 H), 1.31 (br. s, 12 H), 1.55–1.56 (m, 4 H), 3.26 (t, *J* = 7.8 Hz, 4 H), 6.50 (d, *J* = 9.0 Hz, 2 H), 7.35 (d, *J* = 9.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.39, 14.05, 22.68, 26.77, 27.14, 31.68, 50.98, 62.94, 66.48, 72.79, 79.46, 88.29, 88.68, 105.16, 111.16, 134.76, 148.92 ppm. IR (neat): $\tilde{\nu}$ = 2957, 2929, 2858, 2164, 2070, 1602, 1522, 1466, 1406, 1369, 1250, 1197, 1138, 842 cm^{-1}. HR-EI-MS *m*/*z* (%): calcd. for $C_{27}H_{39}NSi^+$: 405.2846; found 405.2846 (90, [M]$^+$).

31: R_f = 0.1 (SiO_2, heptane/CH_2Cl_2, 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88–0.92 (m, 12 H), 1.31 (br. s, 24 H), 1.55–1.57 (m, 8 H), 3.27 (t, *J* = 7.7 Hz, 8 H), 6.51 (d, *J* = 8.9 Hz, 4 H), 7.36 (d, *J* = 9.0 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.06, 22.70, 26.79, 27.17, 31.70, 51.01, 64.88, 67.63, 73.37, 80.22, 105.17, 111.23, 134.88, 148.95 ppm. IR (neat): $\tilde{\nu}$ = 2924, 2855, 2175, 2062, 1592, 1519, 1464, 1404, 1364, 1292, 1256, 1188, 1110, 977, 810 cm^{-1}. HR-EI-MS *m*/*z* (%): calcd. for $C_{44}H_{60}N_2^+$: 616.4751; found 616.4760 (100, [M]$^+$).

4,4′-(Dodeca-1,3,5,7,9,11-hexayne-1,12-diyl)bis(*N*,*N*-dihexylaniline) (8) and 9-[4-(*N*,*N*-Dihexylamino)phenyl]nona-2,4,6,8-tetrayn-1-ol (32): K_2CO_3 (157 mg, 1.13 mmol) and **28** (65 mg, 0.16 mmol) in MeOH/THF, 1:1 (10 mL) were stirred for 1 h at 25 °C. CH_2Cl_2 (20 mL) was added, the organic layer was washed with H_2O (10 mL), dried with $MgSO_4$, and filtered to yield a solution of deprotected **28**, which was directly used in the next step. Prop-2-yn-1-ol (0.14 mL, 135 mg, 2.41 mmol) and Hay catalyst in CH_2Cl_2 (3 mL) were added. The resulting mixture was stirred exposed to air for 2 h at 25 °C and purified by FC (heptane, heptane/AcOEt, 8:2, heptane/AcOEt, 1:1) to afford **8** (20 mg, 38%) as an orange solid and **32** (21 mg, 34%) as a red-brown solid.

8: R_f = 0.3 (SiO_2, heptane/CH_2Cl_2, 9:1); m.p. > 40 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87–0.92 (m, 12 H), 1.25–1.31 (m, 24 H), 1.52–1.57 (m, 8 H), 3.27 (t, *J* = 7.7 Hz, 8 H), 6.51 (d, *J* = 9.1 Hz, 4 H), 7.37 (d, *J* = 9.0 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.03, 22.66, 26.74, 27.12, 31.65, 51.02, 63.99, 64.45, 65.30, 67.71, 73.46, 80.31, 104.31, 111.30, 135.26, 149.19 ppm. IR (neat): $\tilde{\nu}$ = 3734, 3628, 2921, 2852, 2360, 2342, 2133, 2033, 1734, 1594, 1519, 1463, 1406, 1365, 1258, 1194, 1125, 1022, 812 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 280 (48400), 301 (45500), 363 (27900), 393 (42000), 442 (57400), 471 (57700), 517 nm (26700 $M^{-1}cm^{-1}$). HR-FT-MALDI-MS (3-HPA) *m*/*z* (%): calcd. for $C_{48}H_{60}N_2^+$: 664.4751; found 664.4744 (100, [M]$^+$).

32: R_f = 0.3 (SiO_2, heptane/AcOEt, 8:2); m.p. > 40 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.6 Hz, 6 H), 1.26–1.31 (m, 12 H), 1.55–1.66 (m, 5 H), 3.27 (t, *J* = 7.7 Hz, 4 H), 4.38 (d, *J* = 4.9 Hz, 2 H), 6.50 (d, *J* = 9.1 Hz, 2 H), 7.36 (d, *J* = 9.1 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.23, 22.87, 26.97, 27.36, 31.88, 51.20, 51.89, 63.31, 64.01, 65.03, 67.11, 71.41, 73.24, 77.80, 80.21, 104.74, 111.45, 135.26, 149.37 ppm. IR (neat): $\tilde{\nu}$ = 3349, 2923, 2852, 2360, 2341, 2148, 2089, 1700, 1596, 1519, 1464, 1404, 1364, 1294, 1257, 1228, 1186, 1101, 1068, 1016, 884, 810 cm^{-1}. HR-FT-MALDI-MS (3-HPA) *m*/*z* (%): calcd. for $C_{27}H_{34}NO^+$: 388.2635; found 388.2633 (100, [M + H]$^+$).

2-[2-(4-Cyanophenyl)-1,2-(di-1,3-dithiol-2-ylideneethyl)]-3,6-bis(dicyanomethylene)-7-[4-(dimethylamino)phenyl]-4,5-(di-1,3-dithiol-2-ylidene)-1,7-octadiene-1,1,8,8-tetracarbonitrile (7): Tetrayne **6** (6 mg, 0.018 mmol), TCNE (11 mg, 0.089 mmol), and TTF (18 mg, 0.089 mmol) were dissolved in CH_2Cl_2/MeCN, 1:1 (6 mL). The resulting solution was stirred for 18 h at 50 °C and purified by FC (CH_2Cl_2, CH_2Cl_2/EtOAc, 95:5, CH_2Cl_2/EtOAc, 9:1) to give **7** as a black metallic-like solid (10 mg, 58%); R_f = 0.22 (SiO_2, CH_2Cl_2/EtOAc, 9:1); m.p. > 221 °C (decomp.). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 3.16, 3.19 (s, 6 H), 6.47–6.50 (m, 1 H), 6.59–6.61 (m, 1 H), 6.77–6.83 (m, 3 H), 7.11 (d, *J* = 6.5 Hz, 1 H), 7.17 (d, *J* =

6.5 Hz, 1 H), 7.20–7.24 (m, 2 H), 7.31 (d, J = 6.5 Hz, 1 H), 7.38 (d, J = 6.5 Hz, 1 H), 7.57 (d, J = 9.0 Hz, 2 H), 7.89–7.95 (m, 3 H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 40.28, 40.37, 70.69, 70.77, 71.57, 71.97, 75.31, 75.94, 109.88, 110.17, 111.57, 112.10, 112.45, 112.51, 112.61, 112.84, 113.36, 114.64, 114.86, 115.29, 115.33, 115.36, 115.49, 115.61, 115.64, 115.73, 115.80, 115.91, 116.02, 116.07, 116.23, 116.35, 116.41, 116.45, 117.10, 117.31, 117.43, 117.62, 118.39, 118.67, 118.95, 119.05, 119.11, 119.32, 120.37, 120.61, 122.27, 123.49, 125.55, 125.68, 125.81, 125.87, 126.44, 128.97, 129.13, 129.62, 129.68, 130.47, 130.83, 131.82, 131.94, 133.50, 134.07, 140.68, 141.05 ppm. IR (neat): $\tilde{\nu}$ = 3066, 2920, 2851, 2199, 1600, 1486, 1435, 1320, 1208, 1170, 1018, 1000, 941, 901, 848, 817 cm^{-1}. UV/Vis (CH_2Cl_2): 402 (sh, 41000), 459 nm (117000 M^{-1} cm^{-1}). HR-MALDI-MS (3-HPA) m/z (%): calcd. for $C_{47}H_{23}N_{10}S_8^+$: 982.9867; found 982.9850 (100, $[M + H]^+$).

3,8-Bis(dicyanomethylene)-2,9-bis[4-(dimethylamino)phenyl]-1,9-decadiene-4,6-diyne-1,1,10,10-tetracarbonitrile (36): The title compound was prepared from tetrayne **1** (30 mg, 0.09 mmol) and TCNE (23 mg, 0.18 mmol) in CH_2Cl_2 (25 mL), according to the general method. The mixture was stirred for 12 h at 25 °C. After that time, additional TCNE (10 mg, 0.08 mmol) was added and the mixture was stirred for 5 h at 25 °C. FC (CH_2Cl_2/EtOAc, 99:1) gave **36** as a black metallic-like solid (29 mg, 55%). R_f = 0.34 (SiO_2, CH_2Cl_2/EtOAc, 99:1); m.p. > 260 °C (decomp.). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ = 3.11 (s, 12 H), 6.68 (d, J = 9.3 Hz, 4 H), 7.62 (d, J = 9.3 Hz, 4 H) ppm. ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): δ = 40.21, 72.59, 83.63, 92.76, 100.19, 109.22, 110.15, 112.54, 113.41, 113.95, 116.16, 132.27, 147.91, 154.82, 156.36 ppm. IR (neat): $\tilde{\nu}$ = 2921, 2863, 2214, 2136, 1606, 1537, 1480, 1455, 1386, 1355, 1308, 1217, 1175, 1144, 1059, 1003, 990, 939, 898, 825, 797, 743 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 294 (29400), 311 (sh, 28600), 362 (26300), 391 (33200), 471 (62300), 642 nm (4600 M^{-1} cm^{-1}). HR-MALDI-MS (3-HPA) m/z (%): calcd. for $C_{36}H_{20}N_{10}^-$: 592.1881; found 592.1872 ($[M]^-$). $C_{36}H_{20}N_{10}$ (592.62): calcd. C 72.96, H 3.40, N 23.64; found C 73.73, H 3.63, N 23.15.

2-[4-(Dihexylamino)phenyl]-3-{10-[4-(dihexylamino)phenyl]-1,3,5,7,9-decapentayn-1-yl}-1,3-butadiene-1,1,4,4-tetracarbonitrile (37): The title compound was prepared from **8** (17 mg, 0.026 mmol) and TCNE (2.5 mg, 0.02 mmol) in CH_2Cl_2 (6 mL), according to the general method. The mixture was stirred for 5 h, the residue was preadsorbed on SiO_2, and purified by FC (pentane, pentane/CH_2Cl_2, 1:1, pentane/CH_2Cl_2, 3:7, CH_2Cl_2) to yield **37** as a green solid (10 mg, 65%). R_f = 0.8 (SiO_2, CH_2Cl_2); m.p. > 40 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88–0.94 (m, 12 H), 1.25–1.38 (m, 24 H), 1.54–1.64 (m, 8 H), 3.29 (t, J = 7.8 Hz, 4 H), 3.40 (t, J = 7.8 Hz, 4 H), 6.52 (d, J = 9.1 Hz, 2 H), 6.68 (d, J = 9.4 Hz, 2 H), 7.40 (d, J = 9.0 Hz, 2 H), 7.70 (d, J = 9.4 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.03, 22.64, 22.67, 26.69, 26.74, 27.16, 27.33, 31.56, 31.66, 51.04, 51.55, 60.60, 63.92, 67.43, 69.38, 70.28, 72.78, 73.66, 74.54, 83.13, 84.51, 98.27, 99.72, 103.30, 110.01, 110.91, 111.40, 112.23, 113.39, 114.30, 116.43, 132.64, 135.67, 149.20, 149.73, 153.26, 157.87 ppm (37 out of 38). IR (neat): $\tilde{\nu}$ = 2954, 2924, 2854, 2214, 2170, 2004, 1736, 1590, 1524, 1485, 1445, 1406, 1349, 1323, 1293, 1258, 1184, 1170, 1084, 989, 813 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 255 (48300), 332 (48000), 408 (41000), 474 (67000), 639 nm (18500 M^{-1} cm^{-1}). HR-FT-MALDI-MS (3-HPA) m/z (%): calcd. for $C_{54}H_{61}N_6^+$: 793.4952; found 793.4938 (80, $[M + H]^+$).

3,12-Bis(dicyanomethylene)-2,13-bis[4-(dihexylamino)phenyl]-1,13-tetradecadiene-4,6,8,10-tetrayne-1,1,14,14-tetracarbonitrile (38): The title compound was prepared from **8** (32 mg, 0.048 mmol) and TCNE (13 mg, 0.098 mmol) in CH_2Cl_2 (7 mL), according to the general method. The mixture was stirred for 18 h and purified by FC (heptane, heptane/CH_2Cl_2, 1:1, CH_2Cl_2) to give **38** as a dark brown solid (39 mg, 88%). R_f = 0.5 (SiO_2, CH_2Cl_2); m.p. 161–163 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–0.94 (m, 12 H), 1.22–1.38 (m, 24 H), 1.60–1.67 (m, 8 H), 3.41 (t, J = 7.8 Hz, 8 H), 6.69 (d, J = 9.6 Hz, 4 H), 7.69 (d, J = 9.4 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.02, 22.63, 26.67, 27.34, 31.55, 51.61, 67.49, 72.39, 72.58, 78.29, 96.15, 100.17, 109.54, 110.52, 112.42, 113.42, 114.17, 116.28, 132.65, 148.42, 153.45, 156.76 ppm. IR (neat): $\tilde{\nu}$ = 2925, 2854, 2359, 2215, 1724, 1601, 1487, 1455, 1414, 1351, 1259, 1184, 1092, 1015, 865, 796 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 281 (22800), 297 (22800), 318 (23700), 367 (24300), 381 (sh, 22000), 419 (23600), 460 nm (38900 M^{-1} cm^{-1}). HR-FT-MALDI-MS (3-HPA) m/z (%): calcd. for $C_{60}H_{61}N_{10}^+$: 921.5075; found 921.5075 (54, $[M + H]^+$).

3,12-Bis(dicyanomethylene)-2,13-bis[4-(dihexylamino)phenyl]-4,5,10,11-tetra-(1,3-dithiol-2-ylidene)-1,13-tetradecadiene-6,8-diyne-1,1,14,14-tetracarbonitrile (39): The title compound was prepared from **38** (6 mg, 0.007 mmol), according to the general method. The mixture was stirred for 6 h at 50 °C and purified by FC (CH_2Cl_2, CH_2Cl_2/AcOEt, 98:2, CH_2Cl_2/AcOEt, 9:1, CH_2Cl_2/AcOEt, 1:1) to give **39** as a brown solid (5 mg, 58%). R_f = 0.8 (SiO_2, CH_2Cl_2/AcOEt, 95:5); m.p. 252–254 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72–0.90 (m, 12 H), 1.26–1.43 (m, 24 H), 1.62 (br. s, 8 H), 3.39 (br. s, 8 H), 6.62–6.75 (m, 8 H), 6.99–7.10 (m, 4 H), 7.70–8.10 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $C_2D_2Cl_4$): δ = 14.46, 22.96, 26.96, 27.70, 31.84, 51.66, 71.50, 71.60, 74.46, 99.24, 112.58, 112.85, 114.00, 114.36, 115.15, 116.10, 121.70, 122.14, 123.80, 128.71, 132.92, 133.19, 148.63, 148.99, 149.36, 153.63, 153.97, 154.07, 156.20, 156.39, 161.12, 165.41 ppm.[56] IR (neat): $\tilde{\nu}$ = 2959, 2918, 2850, 2360, 2342, 2209, 1727, 1601, 1489, 1456, 1365, 1259, 1182, 1089, 1016, 864, 796 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 228 (24600), 244 (19100), 463 (40100), 484 nm (39900 M^{-1} cm^{-1}). HR-FT-MALDI-MS (3-HPA) m/z (%): calcd. for $C_{72}H_{68}N_{10}S_8Na^+$: 1351.3286; found 1351.3270 (100, $[M + Na]^+$).

3,8,9,12-Tetrakis(dicyanomethylene)-2,13-bis[4-(dihexylamino)-phenyl]-4,5,10,11-tetra-(1,3-dithiol-2-ylidene)-1,13-tetradecadien-6-yne-1,1,14,14-tetracarbonitrile (40): The title compound was prepared from **39** (20 mg, 0.015 mmol) and TCNE (7 mg, 0.054 mmol) in CH_2Cl_2 (5 mL), according to the general method. The mixture was stirred for 18 h and purified by FC (CH_2Cl_2, CH_2Cl_2/AcOEt, 98:2, CH_2Cl_2/AcOEt, 95:5, CH_2Cl_2/AcOEt, 9:1, CH_2Cl_2/AcOEt, 8:2) to afford **40** as a dark brown solid (21 mg, 96%). R_f = 0.3 (SiO_2, CH_2Cl_2/AcOEt, 95:5); m.p. 217–219 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (br. s, 12 H), 1.26–1.35 (m, 24 H), 1.64 (br. s, 8 H), 3.25–3.55 (m, 8 H), 6.74–6.77 (m, 4 H), 7.10–7.32 (m, 8 H), 7.70–8.10 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $C_2D_2Cl_4$): δ = 14.09, 22.68, 26.75, 27.43, 31.60, 51.59, 77.30, 111.61, 112.24, 112.65, 112.86, 114.03, 114.60, 114.85, 115.05, 115.27, 116.32, 133.11, 133.15, 146.96, 147.36, 147.39, 147.81, 153.62, 153.88 ppm.[56] IR (neat): $\tilde{\nu}$ = 3072, 2923, 2853, 2359, 2341, 2205, 2096, 1599, 1487, 1444, 1412, 1344, 1210, 1179, 983, 900, 818 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 252 (42200), 281 (sh, 30700), 458 (115200), 581 nm (sh, 21100 M^{-1} cm^{-1}). HR-FT-MALDI-MS (3-HPA) m/z: calcd. for $C_{78}H_{69}N_{14}S_8^+$: 1457.3590; found 1457.3600 (100, $[M + H]^+$).

4,4′-(1,3,5,7,9,11-Dodecahexayne-1,12-diyl)bis(*N*,*N*-diisopropylaniline) (9): To a solution of the TES-protected alkyne **33** (82 mg, 0.226 mmol) in THF (8 mL), nBu$_4$NF (0.45 mL, 118 mg, 0.45 mmol, 1 M in THF) was added. The mixture was stirred for 20 min at 0 °C, diluted with CH_2Cl_2, and filtered through a plug (SiO_2; CH_2Cl_2). The resulting solution of deprotected **33** was con-

centrated in vacuo to a volume of ca. 20 mL and was directly used in the next step. Hay catalyst in CH_2Cl_2 (5 mL) was added and the resulting mixture stirred exposed to air for 2 h at 25 °C. The solvent was evaporated, the residue adsorbed on SiO_2 and purified by FC (heptane, heptane/AcOEt, 9:1, heptane/AcOEt, 8:2, heptane/AcOEt, 1:1, AcOEt) to afford **9** (36 mg, 65%) as a red solid. R_f = 0.3 (SiO_2, heptane/AcOEt, 8:2); m.p. > 40 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (d, J = 6.9 Hz, 24 H), 3.86–3.95 (m, 4 H), 6.71 (d, J = 9.2 Hz, 4 H), 7.36 (d, J = 9.1 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.98, 47.52, 63.95, 64.43, 65.27, 67.68, 73.50, 80.19, 105.10, 114.96, 134.64, 149.55 ppm. IR (neat): $\tilde{\nu}$ = 2962, 2924, 2852, 2132, 2032, 1588, 1515, 1462, 1420, 1371, 1328, 1296, 1260, 1185, 1155, 1115, 1018, 816 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 282 (51400), 292 (48400), 299 (sh, 45500), 363 (30200), 393 (44300), 440 (56000), 469 (54000), 515 nm (24100 M^{-1} cm^{-1}). HR-ESI-TOF-MS (CH_2Cl_2/MeOH) *m/z* (%): calcd. for $C_{36}H_{37}N_2^+$: 497.2951; found 497.2940 (22, $[M + H]^+$).

2-[4-(Diisopropylamino)phenyl]-3-{10-[4-(diisopropylamino)phenyl]-1,3,5,7,9-decapentayn-1-yl}-1,3-butadiene-1,1,4,4-tetracarbonitrile (41): The title compound was prepared from **9** (32 mg, 0.064 mmol) and TCNE (6 mg, 0.046 mmol) in CH_2Cl_2 (18 mL), according to the general method. The mixture was stirred for 5 h and purified by FC (pentane/AcOEt, 8:2, pentane/AcOEt, 1:1) to give **41** as a green solid (24 mg, 83%). R_f = 0.6 (SiO_2, heptane/AcOEt, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 (d, J = 6.9 Hz, 12 H), 1.39 (d, J = 6.9 Hz, 12 H), 3.88–3.98 (m, 2 H), 4.05–4.14 (m, 2 H), 6.72 (d, J = 9.1 Hz, 2 H), 6.88 (d, J = 9.5 Hz, 2 H), 7.38 (d, J = 9.1 Hz, 2 H), 7.69 (d, J = 9.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.77, 20.85, 20.92, 21.03, 47.48, 47.73, 48.46, 48.70, 60.52, 63.82, 67.32, 69.26, 70.12, 72.71, 73.61, 74.40, 83.00, 84.25, 98.15, 99.58, 103.80, 109.89, 110.78, 113.28, 114.15, 114.63, 114.79, 116.29, 131.81, 131.94, 134.76, 134.95, 148.95, 149.80, 153.33, 157.56 ppm. IR (neat): $\tilde{\nu}$ = 2963, 2924, 2852, 2214, 2154, 2027, 1734, 1596, 1484, 1445, 1371, 1333, 1297, 1260, 1188, 1153, 1088, 1014, 794 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 255 (40500), 332 (37000), 349 (36000), 409 (33900), 472 (54300), 624 nm (15100 M^{-1} cm^{-1}). HR-ESI-TOF-MS (CH_2Cl_2/MeOH) *m/z* (%): calcd. for $C_{42}H_{37}N_6^+$: 625.3074; found 625.3071 (51, $[M + H]^+$).

3,12-Bis(dicyanomethylene)-2,13-bis[4-(diisopropylamino)phenyl]-1,13-tetradecadiene-4,6,8,10-tetrayne-1,1,14,14-tetracarbonitrile (42): The title compound was prepared from **41** (14 mg, 0.022 mmol) and TCNE (6 mg, 0.045 mmol) in CH_2Cl_2 (5 mL), according to the general method. The mixture was stirred for 18 h and purified by FC (pentane/AcOEt, 1:1, AcOEt/CH_2Cl_2, 95:5, AcOEt/CH_2Cl_2, 9:1) to give **42** as a brown solid (11 mg, 65%). R_f = 0.5 (SiO_2, heptane/AcOEt, 1:1); m.p. 130–132 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40 (d, J = 6.9 Hz, 24 H), 4.06–4.15 (m, 4 H), 6.89 (d, J = 9.6 Hz, 4 H), 7.67 (d, J = 9.4 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.87, 20.96, 48.66, 48.86, 67.46, 72.30, 72.63, 78.24, 96.05, 99.96, 109.35, 110.32, 113.21, 113.93, 114.69, 114.79, 116.08, 131.70, 131.82 148.05, 153.34, 156.34 ppm. IR (neat): $\tilde{\nu}$ = 2965, 2931, 2359, 2214, 2178, 2073, 1598, 1482, 1445, 1374, 1337, 1309, 1260, 1218, 1188, 1096, 1013, 791 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 282 (25600), 297 (25600), 318 (26100), 366 (27400), 378 (sh, 24200), 418 (25300), 461 nm (42900 M^{-1} cm^{-1}). HR-FT-MALDI-MS (3-HPA) *m/z* (%): calcd. for $C_{48}H_{37}N_{10}^+$: 753.3197; found 753.3205 (55, $[M + H]^+$).

3,12-Bis(dicyanomethylene)-2,13-bis[4-(diisopropylamino)phenyl]-4,5,10,11-tetra-1,3-dithiol-2-ylidene-1,13-tetradecadiene-6,8-diyne-1,1,14,14-tetracarbonitrile (43): The title compound was prepared from **42** (8 mg, 0.011 mmol), according to the general method. The mixture was stirred for 4 h at 50 °C and purified by FC (heptane/AcOEt, 1:1, heptane/AcOEt, 2:8) to give **43** as a brown solid (8 mg, 65%). R_f = 0.4 (SiO_2, heptane/AcOEt, 2:8); m.p. 205–208 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24–1.60 (m, 24 H), 3.95–4.25 (m, 4 H), 5.10–5.40 (m, 4 H), 6.56–6.62 (m, 2 H), 6.83–6.90 (m, 4 H), 7.00–7.20 (m, 2 H), 7.79–8.00 (m, 4 H) ppm.[56] ^{13}C NMR (75 MHz, $CDCl_3$): not available due to low solubility. IR (neat): $\tilde{\nu}$ = 3069, 2922, 2852, 2359, 2205, 2103, 1717, 1598, 1538, 1445, 1366, 1339, 1308, 1260, 1216, 1186, 1116, 1014, 796 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 230 (18900), 460 (38300), 479 nm (sh, 36000 M^{-1} cm^{-1}). HR-ESI-MS (CH_2Cl_2/MeOH) *m/z* (%): calcd. for $C_{60}H_{45}N_{10}S_8^+$: 1161.1589; found 1161.1594 (100, $[M + H]^+$).

Supporting Information (see also the footnote on the first page of this article): Experimental procedures and spectra (^{1}H NMR, CD/UV/Vis; 16 pages).

Acknowledgments

This work was supported by the Swiss ETH Research Council and the German Fonds der Chemischen Industrie. We thank Dr. J. L. Alonso-Gómez and P. Rivera-Fuentes (ETHZ) for many fruitful discussions and Dr. Carlo Thilgen (ETHZ) for his help with the nomenclature of the compounds described in this paper.

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[57] Specific optical rotatory power was measured at very low concentrations (ca. 0.001 $mg\,mL^{-1}$) due to low solubility, making it prone to a relatively large error.

Received: January 11, 2010
Published Online: March 17, 2010

