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One-Pot Access to Push–Pull Oligoenes by Sequential [2 + 2] Cycloaddition–Retroelectrocyclization Reactions

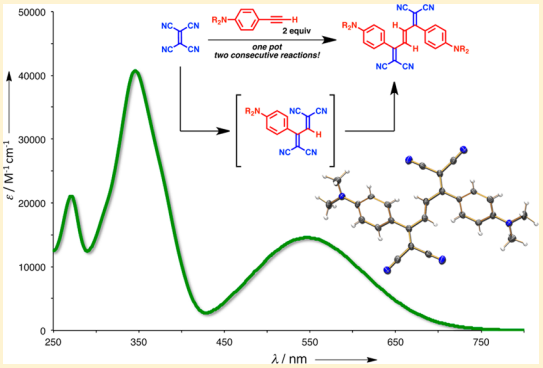
Govindasamy Jayamurugan,[†] Aaron D. Finke,[†] Jean-Paul Gisselbrecht,[‡] Corinne Boudon,[‡] W. Bernd Schweizer,[†] and François Diederich*[,†]

[†]Laboratorium für Organische Chemie, ETH-Zürich , Hönggerberg, HCI, CH-8093 Zürich, Switzerland

[‡]Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, Institut de Chimie–UMR 7177, C.N.R.S., Université de Strasbourg, 4 rue Blaise Pascal, 67081 Strasbourg Cedex, France

Supporting Information

ABSTRACT: The formal [2 + 2] cycloaddition–retroelectrocyclization reaction was employed as the key transformation to obtain donor-substituted, π-conjugated polycyanohexa-1,3,5-trienes (TCHTs and PCHTs) and polycyanoocta-1,3,5,7-tetraenes from donor-substituted tetracyanobuta-1,3-dienes (TCBDs) and electron-rich alkynes. These push–pull-substituted oligoene chromophores were also accessed in good yield from tetracyanoethylene and donor-substituted alkynes by using a one-pot protocol. All bis-(*N*,*N*-dialkylanilino) donor-substituted push–pull trienes and tetraenes showed better electron-accepting potency and lower HOMO–LUMO gaps than the corresponding TCBDs, as evidenced by optical and electrochemical studies.



Oligoenes are fully conjugated fragments of polyacetylene and constitute some of the simplest "molecular wires".[1] Despite their presence in natural products[2] and potential use in organic electronic applications,[3] the study of oligoenes is hampered by a number of issues, including product instability and low solubility. One recent strategy to overcome these problems was reported by Nuckolls and co-workers, who showed that decoration of polyenes with cyano groups leads to lowered HOMO energies and greater chemical stability with respect to oxidative decomposition.[4]

Since 2005, expanding on the earlier work by Bruce and others,[5] we have developed a new class of chromophores: donor-substituted 1,1,4,4-tetracyanobutadienes (TCBDs).[6] These chromophores are easily synthesized by a click-type formal [2 + 2] cycloaddition–retroelectrocyclization (CA–RE) of donor-substituted alkynes and tetracyanoethylene (TCNE). Donor-substituted TCBDs are nonplanar and thermally robust; they feature facile electrochemical reduction, strong charge-transfer bands in the vis/near-IR (NIR) region, and possess high third-order optical nonlinearities. A TCBD derivative has been successfully integrated into silicon–organic hybrid slot waveguides.[7] However, the chemistry of TCBDs themselves has been relatively unexplored. We recently reported that the anilino group of donor-substituted TCBDs can be synthetically elaborated to form new molecular entities.[8] To date, there have only been a few efforts to explore the chemistry of the *acceptor* unit of TCBDs. Previous work in our group found that donor-substituted pentacyanobutadienes, prepared by a CA–RE reaction between a donor-substituted cyanoalkyne and TCNE, are reactive with donor-substituted alkynes; however, their chemistry is not limited to CA–RE-type transformations.[9] Herein, we demonstrate that the terminal dicyanovinyl moiety of donor-substituted TCBDs reacts cleanly in the CA–RE reaction with donor-substituted alkynes to give cyano-rich hexa-1,3,5-trienes and octa-1,3,5,7-tetraenes. We also show that such oligoenes can be directly synthesized from TCNE in a one-pot, multistep CA–RE reaction in good yield.

First, we tested the CA–RE reactivity of donor-substituted TCBDs[6b] **1a** and **1b** with donor-substituted alkynes **2a–2c** (Table 1). We reasoned that the dicyanovinyl moiety in direct conjugation with the anilino donor moiety would be less electrophilic and less reactive due to steric encumbrance.[9a,10] Indeed, TCBDs **1a** and **1b** both reacted cleanly with alkynes **2a** and **2b** at room temperature in $CHCl_3$ to give 1,1,6,6-tetracyano-1,3,5-hexatrienes (TCHTs) **3a–3c** in good yield and exclusively in form of the 3*E*-isomer. We found that less electron-rich alkynes, such as 1-ethynyl-4-methoxybenzene and 3-[4-(dimethylamino)phenyl]propiolonitrile, do not undergo a CA–RE reaction with **1a**. However, the synthesis of 1,1,3,6,6-pentacyano-1,3,5-hexatrienes (PCHTs) **4** could be achieved by increasing the electron richness of the alkyne upon replacement of the *N*,*N*-dimethylamino with a pyrrolidinyl group.[11] Thus, pyrrolidinyl-substituted cyanoalkyne **2c** reacted with TCBD **1a**, but only at high temperatures (120 °C in 1,1,2,2-tetrachloroethane), to give a mixture of PCHT isomers *Z*-**4a** and *E*-**4b** in low yield.[12]

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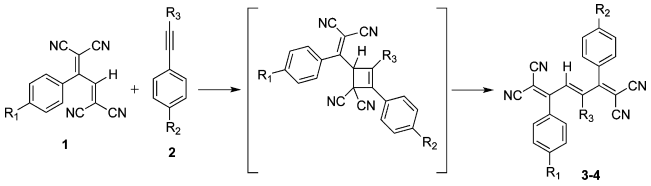
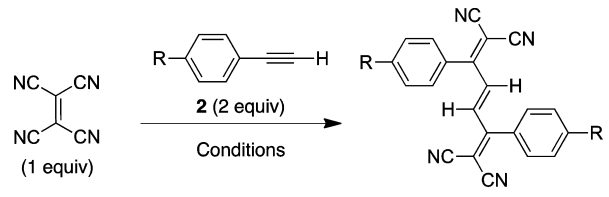
Table 1. Synthesis of 1,1,6,6-Tetracyano-1,3,5-hexatrienes (TCHTs) 3 and 4 from TCBDs 1 with Electron-Rich Alkynes 2



Entry	1	2		Conditions	Product (yield)
	R_1	R_2	R_3		
1	NMe_2 (**1a**)	NMe_2 (**2a**)	H	$CHCl_3$, 25 °C, 24 h	**3a** (88%)
2	NMe_2 (**1a**)	(**2b**)	H	$CHCl_3$, 25 °C, 24 h	**3b** (90%)
3	OMe (**1b**)	NMe_2 (**2a**)	H	$CHCl_3$, 25 °C, 24 h	**3c** (75%)
4	NMe_2 (**1a**)	(**2c**)	CN	$(CHCl_2)_2$, 120 °C, 24 h	*Z*-**4a** (37%) +*E*-**4b** (5%)

Once we established that TCBDs were reactive in the CA–RE reaction, we envisaged that a reaction between anilinoalkynes and TCNE could form TCHTs in one pot via in situ formation of the TCBD, given an initial stoichiometry of 1 equiv of TCNE to 2 equiv of alkyne (Table 2). Mixing 2

Table 2. One-Pot Synthesis of 1,1,6,6-Tetracyano-1,3,5-hexatrienes (TCHTs)

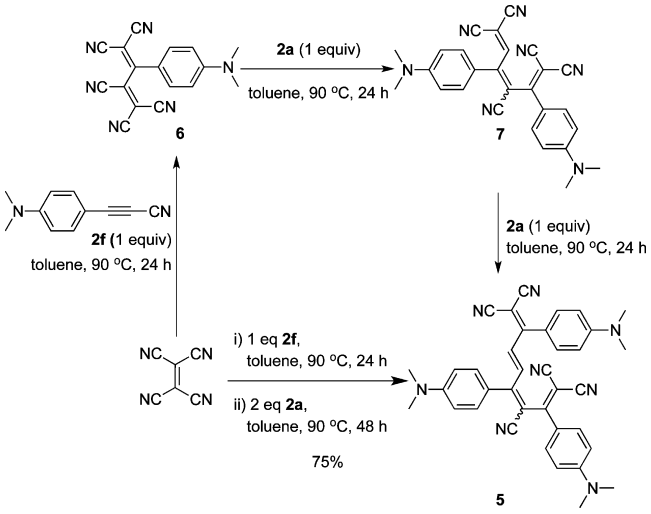


entry	R	conditions	product (yield)
1	NMe_2 (**2a**)	$CHCl_3$, 50 °C, 36 h	**3a** (80%)
2	NBu_2 (**2d**)	$CHCl_3$, 50 °C, 36 h	**3d** (85%)
3	OMe (**2e**)	$(CHCl_2)_2$, 120 °C, 60 h	**3e** (30%) + **1b** (60%)

equiv of alkynes **2a** and **2d** with 1 equiv of TCNE gave TCHTs **3a** and **3d**, respectively, in good yield. Consequent to its decreased electron-donation ability, methoxy-substituted alkyne **2e** was less reactive, requiring higher temperatures and only formed TCHT **3e** in low yield, along with a significant amount (60%) of TCBD **1b**. Again, in all cases, only the 3*E*-isomer was obtained.

We previously reported the preparation of PCHT **7** via a multistep sequence starting from the reaction of **2f** with TCNE to form **6**, followed by a CA–RE reaction of **6** with **2a** (Scheme 1) to give **7** as a 1:1 mixture of 3*E*/3*Z* isomers.[9] Because **7** has a nondonor-conjugated terminal dicyanovinyl group suitable for further elaboration via CA–RE chemistry, we reacted TCNE first with 1 equiv of **2f**, followed by 2 equiv of **2a**, in a one-pot procedure to give pentacyanoocta-1,3,5,7-tetraene (PCOT) **5** in good yield. Adduct **5** was isolated as a mixture of 3*Z*,5*E*/3*E*5*E* isomers in a ratio of 71:29 as measured by ^{1}H NMR; unfortunately, despite multiple attempts by chromatographic methods, the isomers could not be separated.

Scheme 1. Synthesis of 1,1,8,8-Tetracyano-1,3,5,7-tetraenes



Crystals suitable for X-ray analysis of **3a**, **3c**, **3d**, **3e**, *Z*-**4a**, *E*-**4b**, and (3*Z*,5*E*)-**5** were prepared (Section 1SI, Supporting Information) to confirm the configuration assigned to each adduct. The central double bond of **3** exclusively has an *E*-configuration when it is unsubstituted, as in **3a**, **3c**, **3d**, and **3e**. By contrast, when the central double bond is substituted, as in hexatrienes *Z*-**4a**, *E*-**4b**, or in the case of one of the two central double bonds in (3*Z*,5*E*)-**5**, a mixture of *E*- and *Z*-isomers is formed (Figure 1). The mixture of PCOT isomers **5** is also stable in solution, and no coalescence in the NMR spectra (500 MHz, 1,1,2,2-tetrachloroethane-d_2) occurs when heating up to 100 °C, indicating a high barrier of isomerization. The high barrier results from the high nonplanarity of the push–pull skeleton (Figure 1d), which strongly reduces the π-conjugation along the pentacyanotetraene backbone and raises the transition state for *E*/*Z* isomerization.[13]

The quinoidal character[14,15] δr of the donor rings of **3a**, **3c**, **3d**, *Z*-**4a**, and *E*-**4b** was determined from the X-ray bond lengths (see Section 2SI, Supporting Information). The quinoidal character of the aniline rings is moderate, with δr values ranging from 0.025 to 0.052. By contrast, the quinoidal character of the methoxyphenyl ring in **3c** is extremely low (0.004), indicative of the lower donor strength of the methoxy group. The bond lengths and bond length alternations of the 1,3,5-triene and 1,3,5,7-tetraene moieties are typical for oligoenes.

The four 3*E*-configured TCHTs **3a**, **3c**, **3d**, and **3e** all adopt a similar conformation in the solid state. The triene moieties are almost, but not fully, planar; the torsion angles between each pair of neighboring alkene bonds range from 15° to 17°. In contrast, the PCHT isomers *Z*-**4a** and *E*-**4b** adopt drastically different conformations in the solid state. The internal cyanoethene-1,2-diyl moiety in *Z*-**4a** is almost orthogonal to the external dicyanovinyl groups (θ = 103–106°), in order to minimize the torsion (and thus maximize the conjugation efficiency) between the anilino rings and the dicyanovinyl groups. In contrast to *Z*-**4a**, which adopts an elongated shape, *E*-**4b** is almost folded onto itself; again, the nearly orthogonal orientation of the central double bond acts to maximize the π-conjugation between the anilino rings and dicyanovinyl groups.

The spectral and electrochemical data for all new compounds were collected. The UV/vis spectra demonstrate the effect of adding additional alkene spacers between the dicyanovinyl

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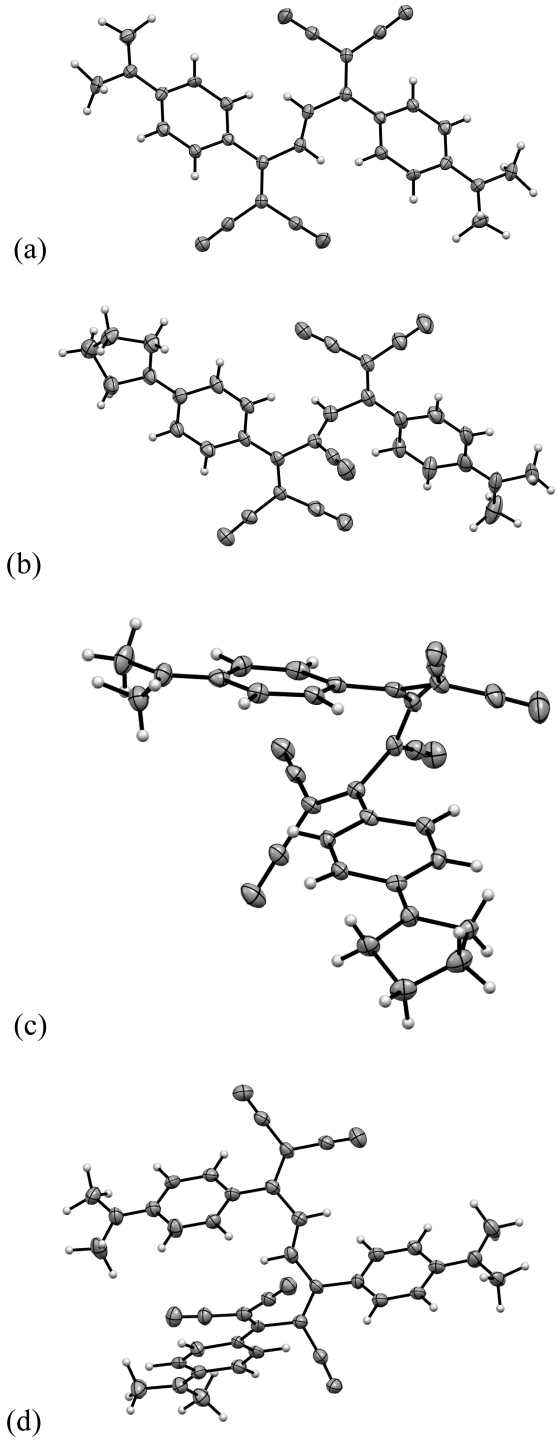

Figure 1. ORTEP of (a) **3a**, (b) *Z*-**4a**, (c) *E*-**4b**, and (d) (3*Z*,5*E*)-**5**. *T* = 100 K. Ellipsoids at 50% probability.

termini (Figure 2). Anilino-substituted TCHTs **3a**−**3d** have similar UV/vis spectra, featuring two major peaks at λ_{max} = 350 nm and λ_{max} = 560 nm. The latter peak corresponds to an intramolecular charge-transfer (ICT) band with extinction coefficients in the range of similar push−pull systems (log ε = 4−4.5). TCHT **3e** has a less pronounced transition at λ_{max} = 420 nm due to its weaker methoxy donor moiety. PCHTs *Z*-**4a** and *E*-**4b** and PCOT **5** have more complex UV/vis spectra (Figure 2b), but the ICT band energies are relatively unaffected.

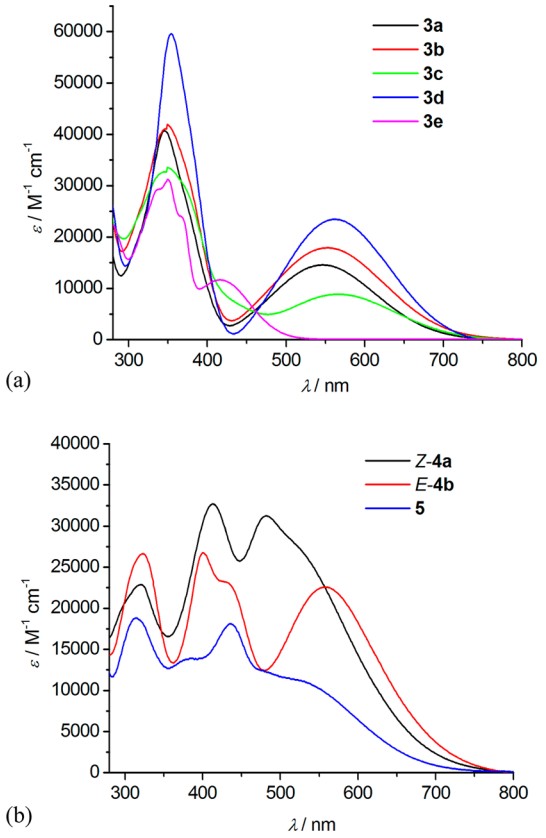

Figure 2. UV/vis absorption spectra of compounds (a) **3a**−**3e**, and (b) *Z*-**4a**, *E*-**4b**, and **5** in CH_2Cl_2 at 298 K; $c \sim 10^{-5}$ M.

The necessity of the anilino donor for ICT was confirmed by monitoring the UV/vis spectra upon protonation with CF_3COOH and subsequent neutralization with NEt_3 (Section 4SI, Supporting Information). TCHT derivatives **3a**−**3d** all display reversible loss of ICT bands upon protonation with CF_3COOH; the ICT band returns quantitatively upon neutralization with NEt_3. The UV/vis spectrum of methoxy-substituted TCHT **3e** is unaffected by protonation or neutralization. PCHTs *Z*-**4a** and *E*-**4b** also react with CF_3COOH to generate much simpler spectra compared to those of the parent compounds, with λ_{max} = 460 nm and λ_{max} = 470 nm for *Z*-**4a** and *E*-**4b**, respectively; however, neutralization with NEt_3 does not regenerate the original spectra, indicating that additional chemistry occurs in the process. PCOT derivative **5**, in contrast to the PCHTs, displays reversible ICT band disappearance upon protonation and subsequent neutralization.

The electrochemistry of the new oligoene derivatives was measured in CH_2Cl_2 + 0.1 M *n*-Bu_4NPF_6 (Section 5SI, Supporting Information; all redox potentials described herein are reported versus Fc/Fc^+ = 0 V). The TCHT and PCHT derivatives all display two well-resolved, reversible one-electron reductions at potentials more positive than that of the TCBD derivative **8** (2,3-bis[4-(dimethylamino)phenyl]buta-1,3-diene-1,1,4,4-tetracarbonitrile)[6a] by ca. 130 mV. This indicates that the additional alkene spacer facilitates reduction of the TCHT. The weaker methoxy donor groups in **3c** and **3e** lead to more positive reduction potentials than those of the anilino-substituted TCHTs. PCHTs *Z*-**4a** and *E*-**4b** display first reduction potentials at −0.73 and −0.71 V, respectively, which are more positive than those of the anilino-TCHTs by

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about 200 mV, on account of the additional electron-accepting cyano group. Interestingly, the presence of one extra alkene spacer in PCOT **5** does not lead to an expected facilitation of the first reduction compared to the PCHTs; instead, a two-electron reduction at even more negative potential (−0.86 V) was observed. This again is a consequence of the profound nonplanarity of the push−pull-substituted tetraene. In this case, the polyene appears to stabilize the *second* reduction. In fact, this trend holds true for the whole series described in this study: the potential difference between the first and second reduction potentials of the TCHTs is ca. 300 mV; for the PCHTs, the potential difference is 180 mV; and the two reductions for the PCOT occur simultaneously. Thus, increasing the polyene length acts to stabilize the second reduction rather than the first.

In conclusion, the chemical reactivity of the acceptor dicyanovinyl moieties of TCBDs was elaborated in terms of their participation in CA−RE reactions with donor-substituted alkynes. We prepared a series of donor-substituted, cyano-rich trienes and tetraenes via a one-pot reaction between TCNE and donor-substituted alkynes. These new chromophores feature facilitated reductions compared to their TCBD counterparts and strong intramolecular charge-transfer bands and are easily accessible from simple starting materials. The utility of these polyene chromophores in nonlinear optical applications will be investigated.

EXPERIMENTAL SECTION

General. Reagents and compounds **2a** and **2e** were purchased and used as received. Flash column chromatography (FC) was carried out with SiO_2 60 (particle size 0.040−0.063 mm, 230−400 mesh) and technical solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with SiO_2 60 F_{254}; visualization was with a UV lamp (254 nm). The syntheses of **1a** and **1b**,[6b] **2b**,[16] **2d**,[17] **6**,[18] **7**,[9] and 3-[4-(*N*,*N*-dimethylamino)phenyl]propynenitrile[18] were performed according to the literature. Melting points (m.p.) were measured in open capillaries, and reported values are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured at 20 °C. Chemical shifts are reported in parts per million (ppm) relative to the signal of tetramethylsilane (δ = 0 ppm). Residual solvent signals in the ^{1}H and ^{13}C NMR spectra were used as an internal reference. Coupling constants (J) are given in hertz. The apparent resonance multiplicity is described as s (singlet), d (doublet), t (triplet), m (multiplet), and br. (broad). NMR peaks were assigned by 2D COSY, NOESY, HSQC, and HMBC experiments. Infrared spectra (IR) were recorded on an FTIR spectrometer. UV/vis spectra were recorded in a quartz cuvette with a 1 cm path length. The absorption wavelengths are reported in nanometers with the molar extinction coefficient ε (M^{-1} cm^{-1}) in parentheses; shoulders are indicated as sh. HR-MALDI-MS spectra were measured with 3-hydroxypicolinic acid (3-HPA) and 2-[(2*E*)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix. The signal of the molecular ion (M^+) is reported in m/z units.

3[4-(Pyrrolidin-1-yl)phenyl]propiolonitrile (2c). A solution of alkyne **2b**[16] (7.5 g, 43.8 mmol) in anhydrous THF (50 mL) was cooled to −78 °C, treated dropwise with 1.6 M *n*-BuLi in hexane (4.2 mL, 65.7 mmol), stirred at −78 °C for 1 h, and treated portionwise with a freshly prepared solution of PhOCN[19] (8.97 g, 74.4 mmol) in THF (15 mL).[20] The mixture was stirred at −78 °C for 30 min and at −40 °C for 15 min, warmed to r.t., and diluted with H_2O. The aqueous layer was extracted with EtOAc (3×). The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$, and evaporated. Column chromatography (SiO_2; pentane/EtOAc 9:1) gave **2c** (6.0 g, 70%) as a yellowish brown solid. R_f = 0.60 (SiO_2; pentane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.04 (m, 4 H; $H_2C(3',4')$), 3.33 (m, 4 H; $H_2C(2',5')$), 6.47 (d, J = 8.9 Hz, 2 H; H−C(3,5)), 7.43 ppm (d, J = 9.0 Hz, 2 H; H−C(2,6)); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.6 (C(3′,4′)), 47.7 (C(2′,5′)), 62.4 (C≡C−CN), 86.7 (*C*≡C−CN), 102.0 (C(1)), 106.9 (CN), 111.7 (C(3,5)), 135.3 (C(2,6)), 149.7 ppm (C(4)); IR (ATR) $\tilde{\nu}$ = 2956 (w), 2914 (w), 2858 (m), 2232 (m), 2211 (m), 2123 (m), 1592 (s), 1523 (m), 1481 (m), 1458 (m), 1399 (m), 1350 (m), 1287 (m), 1180 (s), 1159 (m), 1115 (w), 959 (m), 820 cm^{-1} (s); HR-EI-MS m/z (%) 196.0988 (100, $[M]^+$, calcd for $C_{13}H_{12}N_2^+$: 196.1000), 195.0916 (99, $[M - H]^+$), 140.0495 (53), 126.0339 (27), 68.9947 (21).

(*E*)-2,5-Bis[4-(dimethylamino)phenyl]hexa-1,3,5-triene-1,1,6,6-tetracarbonitrile (3a). A solution of **2a** (105 mg, 0.72 mmol) and **1a**[6b] (220 mg, 0.8 mmol) in $CHCl_3$ (30 mL) was stirred at 25 °C for 24 h and evaporated. FC (SiO_2; CH_2Cl_2) gave **3a** (270 mg, 88%) as a purple solid. R_f = 0.24 (SiO_2; CH_2Cl_2); mp 312−313 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.12 (s, 12 H; NMe_2), 6.76 (d, J = 9.1 Hz, 4 H; H−C(3′,5′)), 7.31 (s, 2 H; H−C(3)), 7.47 ppm (d, J = 9.1 Hz, 4 H; H−C(2′,6′)); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 40.2 (NMe_2), 80.1 (C(1)), 111.8 (C(3′,5′)), 113.8 (CN), 114.7 (CN), 118.6 (C(1′)), 132.3 (C(2′,6′)), 141.8 (C(3)), 153.7 (C(4′)), 167.2 ppm (C(2)); IR (ATR) $\tilde{\nu}$ = 2957 (w), 2923 (w), 2851 (w), 2217 (m), 1598 (s), 1539 (w), 1500 (s), 1435 (w), 1379 (m), 1341 (m), 1285 (m), 1233 (w), 1208 (m), 1191 (w), 1174 (w), 1105 (w), 1063 (w), 985 (m), 943 (m), 825 (s), 802 (w), 751 (w), 739 (w), 693 cm^{-1} (w); HR-MALDI-MS m/z (%) 441.1793 (75, $[M + Na]^+$, calcd for $C_{26}H_{22}N_6Na^+$: 441.1804), 419.1976 (74, $[M + H]^+$, calcd for $C_{26}H_{23}N_6^+$: 419.1979), 235.0713 (100).

(*E*)-2-[4-(Dimethylamino)phenyl]-5-[4-(pyrrolidin-1-yl)-phenyl]hexa-1,3,5-triene-1,1,6,6-tetracarbonitrile (3b). A solution of **2b** (55 mg, 0.32 mmol) and **1a** (97 mg, 0.35 mmol) in $CHCl_3$ (30 mL) was stirred at 25 °C for 24 h and evaporated. FC (SiO_2; CH_2Cl_2) gave **3b** (130 mg, 90%) as a black solid. R_f = 0.25 (SiO_2; CH_2Cl_2); mp 280−281 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 2.06 (m, 4 H; $H_2C(3,4)$ of pyrrolidin-1-yl), 3.11 (s, 6 H; NMe_2), 3.42 (m, 4 H; $H_2C(2,5)$ of pyrrolidin-1-yl), 6.68 (d, J = 9.0 Hz, 2 H; H−C(2″,6″)), 6.81 (d, J = 9.1 Hz, 2 H; H−C(2′,6′)), 7.25 (d, J = 15.2 Hz, 1 H; H−C(2)), 7.30 (d, J = 15.2 Hz, 1 H; H−C(3)), 7.48 and 7.49 ppm (2 d, J = 9.1 Hz, 4 H; H−C(2′,6′,2″,6″)); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 26.0 (C(3,4) of pyrrolidin-1-yl), 40.5 (NMe_2), 48.4 (C(2,5) of pyrrolidin-1-yl), 79.7 and 80.8 (C(3,4)), 112.07 and 112.27 (C(3′,5′,3″,5″)), 114.24 and 114.48 (C(1)($CN)_2$), 115.18 and 115.43 (C(6)($CN)_2$), 118.70 and 119.18 (C(1′,1″)), 132.63 and 132.87 (C(2′,6′,2″,6″)), 141.93 and 142.43 (C(3,4)), 151.8 (C(4″)), 154.1 (C(4′)), 167.6 and 167.8 ppm (C(1,6)); IR (ATR) $\tilde{\nu}$ = 2957 (w), 2922 (w), 2864 (w), 2216 (m), 1602 (s), 1538 (w), 1504 (m), 1440 (w), 1401 (m), 1378 (m), 1341 (m), 1281 (w), 1206 (w), 1189 (m), 1105 (w), 1063 (w), 982 (w), 964 (w), 945 (w), 825 (m), 800 (w), 761 (m), 751 (m), 739 (w), 694 cm^{-1} (w); HR-ESI-MS m/z (%) 467.1957 (93, $[M + Na]^+$, calcd for $C_{28}H_{24}N_6Na^+$: 467.1955), 445.2136 (100, $[M + H]^+$, calcd for $C_{28}H_{25}N_6^+$: 445.2135).

(*E*)-2-[4-(Dimethylamino)phenyl]-5-(4-methoxyphenyl)hexa-1,3,5-triene-1,1,6,6-tetracarbonitrile (3c). A solution of **2a** (70 mg, 0.48 mmol) and **1b** (138 mg, 0.53 mmol) in $CHCl_3$ (30 mL) was stirred at 25 °C for 24 h and evaporated. FC (SiO_2; CH_2Cl_2) gave **3c** (147 mg, 75%) as a dark purple, metallic solid. R_f = 0.23 (SiO_2, CH_2Cl_2); mp 277−278 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 3.11 (s, 6 H; NMe_2), 3.91 (s, 3 H; OMe), 6.80 (d, J = 9.1 Hz, 2 H; H−C(2′,6′)), 7.11 (d, J = 8.9 Hz, 2 H; H−C(2″,6″)), 7.20 (d, J = 15.2 Hz, 1 H; H−C(4)), 7.35 (d, J = 15.2 Hz, 1 H; H−C(3)), 7.459 and 7.462 ppm (2d, J = 9.1 Hz, 4 H; H−C(3′,5′,3″,5″)); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 39.9 (NMe_2), 55.6 (OMe), 80.7 (C(1)), 86.2 (C(6)), 111.5 (C(3′,5′)), 112.2 (CN), 113.1 (CN), 113.5 (CN), 114.5 (CN), 114.8 (C(3″,5″)), 118.3 (C(1′)), 123.8 (C(1″)), 131.4 and 132.0 (C(2′,6′,2″,6″)), 140.1 (C(4)), 142.7 (C(3)), 153.6 (C(4′)), 163.1 (C(4″)), 166.4 and 167.8 ppm (C(2,5)); IR (ATR) $\tilde{\nu}$ = 2953 (w), 2912 (w), 2839 (w), 2220 (m), 1601 (s), 1527 (w), 1506 (m), 1441 (w), 1379 (m), 1336 (m), 1306 (w), 1281 (m), 1262 (m), 1211 (w), 1180 (m), 1105 (w), 1029 (w), 982 (w), 951 (w), 840 (w), 828 (m), 805 (w), 740 cm^{-1} (w); HR-ESI-MS m/z (%) 428.1485 (100, $[M + Na]^+$, calcd for $C_{25}H_{19}N_5NaO^+$: 428.1482), 406.1667 (50, $[M + H]^+$,

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calcd for $C_{25}H_{20}N_5O^+$: 445.2135), 344.9848 (74), 304.2616 (99), 262.9819 (83).

(*E*)-2,5-Bis[4-(dibutylamino)phenyl]hexa-1,3,5-triene-1,1,6,6-tetracarbonitrile (3d). A solution of **2d** (466 mg, 0.2 mmol) and TCNE (130 mg, 0.1 mmol) in $CHCl_3$ (30 mL) was stirred at 50 °C for 36 h and evaporated. FC (SiO_2; CH_2Cl_2) gave **3d** (506 mg, 85%) as a purple solid. R_f = 0.49 (SiO_2; CH_2Cl_2); mp 206−207 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.98 (t, J = 7.3 Hz, 12 H; 4 Me), 1.35 − 1.42 (m, 8 H; 4 CH_2Me), 1.60−1.67 (m, 8 H; 2 N(CH$_2$CH_2)$_2$), 3.39 (br. t, J = 7.8 Hz, 8 H; 2 N(CH_2)$_2$), 6.75 (d, J = 9.2 Hz, 4 H; H−C(3′,5′)), 7.27 (s, 2 H; H−C(3)), 7.49 ppm (d, J = 9.1 Hz, 4 H; H−C(2′,6′)); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 14.2 (2 Me), 20.8 (2 CH_2Me), 29.8 (N(CH$_2$CH$_2$)$_2$), 51.4 (N(CH_2)$_2$), 78.9 (C(1)), 111.8 (C(3′,5′)), 114.6 (CN), 115.6 (CN), 118.5 (C(1′)), 133.1 (C(2′,6′)), 142.1 (C(3)), 152.6 (C(4′)), 167.2 ppm (C(2)); IR (ATR) $\tilde{\nu}$ = 2954 (m), 2928 (m), 2862 (w), 2213 (m), 1594 (s), 1533 (w), 1482 (s), 1435 (w), 1411 (m), 1366 (m), 1341 (s), 1289 (w), 1275 (m), 1230 (w), 1205 (m), 1187 (s), 1162 (m), 1105 (m), 991 (w), 976 (w), 925 (w), 820 (s), 798 (w), 763 (w), 738 (w), 692 cm^{-1} (w); HR-ESI-MS m/z (%) 587.3846 (100, $[M + H]^+$, calcd for $C_{38}H_{47}N_6^+$: 587.3857), 338.3414 (75).

(*E*)-2,5-Bis(4-methoxyphenyl)hexa-1,3,5-triene-1,1,6,6-tetracarbonitrile (3e). A solution of **2e** (307 mg, 2.33 mmol) and TCNE (149 mg, 1.16 mmol) in $(CHCl_2)_2$ (10 mL) was stirred at 120 °C for 60 h and evaporated. FC (SiO_2; CH_2Cl_2) gave **3e** (137 mg, 30%) as a red solid and **1b**[6b] (182 mg, 60%). R_f = 0.30 (SiO_2; CH_2Cl_2); mp 271−272 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 3.91 (s, 6 H; OMe), 7.11 (d, J = 8.9 Hz, 4 H; H−C(2′,6′)), 7.26 (s, 2 H; H−C(3)), 7.44 ppm (d, J = 8.9 Hz, 4 H; H−C(3′,5′)); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 55.7 (OMe), 87.0 (C(1)), 112.0 (CN), 113.0 (CN), 114.8 (C(3′,5′)), 123.5 (C(1′)), 131.3 (C(2′,6′)), 141.2 (C(3)), 163.2 (C(4′)), 167.3 ppm (C(2)); IR (ATR) $\tilde{\nu}$ = 3110 (w), 3075 (w), 3038 (w), 2958 (w), 2937 (w), 2913 (w), 2840 (w), 2225 (s), 1601 (s), 1575 (m), 1531 (m), 1507 (s), 1446 (w), 1442 (w), 1426 (w), 1335 (m), 1309 (m), 1285 (s), 1264 (s), 1182 (s), 1127 (w), 1108 (m), 1026 (s), 1011 (m), 992 (m), 972 (w), 959 (w), 843 (s), 830 (m), 793 (w), 741 (m), 697 (w), 632 cm^{-1} (w); HR-ESI-MS m/z (%) 415.1155 (100, $[M + Na]^+$, calcd for $C_{24}H_{16}N_4NaO_2^+$: 415.1165), 344.9838 (52), 304.2606 (63), 268.9981 (53), 262.9811 (57), 186.9787 (41).

(*Z*)-5-[4-(Dimethylamino)phenyl]-2-[4-(pyrrolidin-1-yl)-phenyl]hexa-1,3,5-triene-1,1,3,6,6-pentacarbonitrile (*Z*-4a) and (*E*)-5-[4-(Dimethylamino)phenyl]-2-[4-(pyrrolidin-1-yl)-phenyl]hexa-1,3,5-triene-1,1,3,6,6-pentacarbonitrile (*E*-4b). In a sealed tube, a solution of **2c** (213 mg, 1.1 mmol) and **1a** (270 mg, 1 mmol) in $(CHCl_2)_2$ (10 mL) was stirred at 120 °C for 24 h. Evaporation and FC (SiO_2; CH_2Cl_2 → CH_2Cl_2/EtOAc 98:2) gave *Z*-**4a** (172 mg, 37%) as a bluish-maroon solid and *E*-**4b** (23 mg, 5%) as a brownish-black solid.

Z-**4a**: R_f = 0.48 (SiO_2; CH_2Cl_2/EtOAc 98:2); mp 227.5−228.5 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 2.06 (m, 4 H; H_2C(3,4) of pyrrolidin-1-yl), 3.14 (s, 6 H; NMe_2), 3.46 (m, 4 H; H_2C(2,5) of pyrrolidin-1-yl), 6.67 (d, J = 9.2 Hz, 2 H; H−C(3′,5′)), 6.80 (d, J = 9.3 Hz, 2 H; H−C(3″,5″)), 7.69 (s, 1 H; H−C(4)), 7.75 (d, J = 9.2 Hz, 2 H; H−C(2′,6′)), 7.80 ppm (d, J = 9.3 Hz, 2 H; H−C(2″,6″)); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 25.8 (C(3,4) of pyrrolidin-1-yl), 40.5 (NMe_2), 48.6 (C(2,5) of pyrrolidin-1-yl), 74.5 and 77.1 (C(1,6)), 112.3 and 112.9 (C(3′,5′,3″,5″)), 113.3 (NC−C(3)), 114.9 (CN), 115.0 (CN), 115.4 (CN), 115.5 (CN), 118.0 and 119.1 (C(1′,1″)), 122.0 (C(3)), 133.1 and 133.6 (C(2′,6′,2″,6″)), 150.1 (C(4)), 152.9 (C(4′)), 154.9 (C(4″)), 162.3 and 162.4 ppm (C(2,5)); IR (ATR) $\tilde{\nu}$ = 3018 (w), 2981 (w), 2953 (w), 2924 (w), 2865 (w), 2214 (m), 1603 (s), 1495 (m), 1443 (m), 1409 (m), 1383 (m), 1340 (m), 1209 (m), 1186 (m), 820 (w), 750 cm^{-1} (w); HR-ESI-MS m/z (%) 492.1902 (100, $[M + Na]^+$, calcd for $C_{29}H_{23}N_7Na^+$: 492.1907), 470.2086 (40, $[M + H]^+$, calcd for $C_{29}H_{24}N_7^+$: 470.2088), 344.9843 (93), 262.9815 (100), 173.0783 (95), 158.9966 (78).

E-**4b**: R_f = 0.38 (SiO_2; CH_2Cl_2/EtOAc 98:2); mp 180−181 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 2.09 (m, 4 H; H_2C(3,4) of pyrrolidin-1-yl), 3.13 (s, 6 H; NMe_2), 3.46 (m, 4 H; H_2C(2,5) of pyrrolidin-1-yl), 6.51 (d, J = 9.2 Hz, 2 H; H−C(3′,5′)), 6.62 (d, J = 9.1 Hz, 2 H; H−C(3″,5″)), 7.14 (d, J = 9.1 Hz, 2 H; H−C(2″,6″)), 7.23 (d, J = 9.2 Hz, 2 H; H−C(2′,6′)), 7.87 ppm (s, 1 H; H−C(4)); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 25.3 (C(3,4) of pyrrolidin-1-yl), 40.0 (NMe_2), 48.1 (C(2,5) of pyrrolidin-1-yl), 74.0 and 77.4 (C(1,6)), 111.4 and 112.2 (C(3′,5′,3″,5″)), 113.5 (CN), 113.6 (CN), 114.2 (CN), 114.7 (CN), 115.1 (CN), 119.3 and 119.5 (C(1′,1″)), 122.8 (C(3)), 131.8 and 132.3 (C(2′,6′,2″,6″)), 150.3 (C(4)), 152.2 (C(4′)), 154.1 (C(4″)), 159.8 (C(5)), 162.6 ppm (C(2)); IR (ATR) $\tilde{\nu}$ = 3018 (w), 2981 (w), 2924 (w), 2860 (w), 2214 (m), 1602 (s), 1537 (w), 1491 (s), 1443 (m), 1407 (s), 1375 (m), 1345 (m), 1284 (w), 1209 (m), 1186 (m), 818 (m), 752 (m), 667 cm^{-1} (w); HR-ESI-MS m/z (%) 492.1906 (34, $[M + Na]^+$, calcd for $C_{29}H_{23}N_7Na^+$: 492.1907), 470.2090 (11, $[M + H]^+$, calcd for $C_{29}H_{24}N_7^+$: 470.2088), 420.9703 (33), 344.9844 (54), 262.9813 (61), 256.9645 (100).

(3*E*,5*E*)- and (3*Z*,5*E*)-2,4,7-Tris[4-(dimethylamino)phenyl]-octa-1,3,5,7-tetraene-1,1,3,8,8-pentacarbonitrile ((3*E*,5*E*)/(3*Z*,5*E*)-5). A solution of 3-[4-(dimethylamino)phenyl]propiolonitrile (129 mg, 0.76 mmol) and TCNE (97 mg, 0.76 mmol) in toluene (30 mL) was stirred at 90 °C for 24 h, treated with **2a** (220 mg, 1.52 mmol), and stirred at 90 °C for 48 h. Evaporation and FC (SiO_2; CH_2Cl_2) gave a 7:3 mixture of (3*E*,5*E*)/(3*Z*,5*E*)-**5** (335 mg, 75%) as a brownish-black solid. R_f = 0.64 (SiO_2; CH_2Cl_2/EtOAc 98:2); ^{1}H NMR (400 MHz, CD_2Cl_2; (3*E*,5*E*)/(3*Z*,5*E*) 7:3) δ = 3.02 and 3.06 (2s, 1.8 and 4.2 H; NMe_2), 3.10 (s, 6 H; NMe_2), 3.11 (s, 6 H; NMe_2), 6.64 (d, J = 9.0 Hz, 0.6 H) and 6.77 (d, J = 9.1 Hz, 1.4 H), 6.71 (d, J = 9.3 Hz, 2 H), 6.86 (d, J = 9.0 Hz, 2 H) (3x H−C(3′,5′)), 6.80 (d, J = 15.2 Hz, 0.7 H), 7.19 (d, J = 15.2 Hz, 0.7 H), 7.24 (d, J = 15.2 Hz, 0.3 H), 7.50 (d, J = 15.1 Hz, 0.3 H) (H−C(5,6)), 7.13 (d, J = 9.0 Hz, 0.6 H), 7.36 (d, J = 9.1 Hz, 1.4 H), 7.50 (d, J = 9.0 Hz, 1.4 H), 7.52 (d, $J \approx$ 8.3 Hz, 0.6 H), 7.65 (d, J = 9.2 Hz, 1.4 H) 7.70 ppm (d, J = 9.2 Hz, 0.6 H) (3× H−C(2′,6′); ^{13}C NMR (100 MHz, CD_2Cl_2; (3*E*,5*E*)/(3*Z*,5*E*) 7:3) signals of (3*E*,5*E*): δ = 40.4, 40.5, 40.5, 76.8, 79.7, 80.3, 109.2, 114.4, 115.3, 115.4, 115.7, 118.0, 119.0, 119.2, 121.7, 132.4, 132.5, 133.4, 139.8, 142.4, 153.3, 153.9, 155.0, 161.7, 163.1, 168.7, signals of (3*Z*,5*E*, two signals are overlapping) δ = 40.44, 40.49, 78.1, 80.3, 108.6, 112.0, 114.3, 115.1, 115.4, 116.7, 119.4, 119.7, 120.4, 131.9, 132.6, 133.1, 139.7, 144.7, 152.8, 154.0, 154.6, 161.4, 164.5, 168.7 ppm; IR (ATR) $\tilde{\nu}$ = 2911 (w), 2864 (w), 2811 (w), 2214 (m), 1601 (s), 1542 (w), 1489 (m), 1438 (w), 1377 (m), 1340 (m), 1209 (m), 1190 (m), 1167 (m), 944 (w), 820 cm^{-1} (w); HR-ESI/MALDI-MS (dual, DCTB as matrix) m/z (%) 588.2750 (100, $[M]^+$, calcd for $C_{37}H_{32}N_8^+$: 588.2746).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra, quinoidal character, and electrochemistry of all new compounds; and crystal structure data for compounds **3a**, **3c**, **3d**, **3e**, *Z*-**4a**, *E*-**4b**, and (3*E*,5*E*)-**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: diederich@org.chem.ethz.ch.

Notes

The authors declare no competing financial interest.

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