Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Charge-Transfer Chromophores by Cycloaddition-Retroelectrocyclization: Multivalent Systems and Novel Cascade Reactions

Milan Kivala,[a] Corinne Boudon,[b] Jean-Paul Gisselbrecht,[b]
Paul Seiler,[a] Maurice Gross,[b] François Diederich*[a]

[a] Prof. Dr. F. Diederich, M. Kivala, P. Seiler
Laboratorium für Organische Chemie
ETH Zürich
Hönggerberg, HCI, CH-8093 Zürich (Switzerland)
Fax: (+41) 44 632 1109
E-mail: diederich@org.chem.ethz.ch

[b] Prof. Dr. M. Gross, Dr. C. Boudon, Dr. J.-P. Gisselbrecht
Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide
Institut de Chimie – LC3 – UMR 7177, C.N.R.S, Université Louis Pasteur
4, rue Blaise Pascal, F-67000, Strasbourg (France)

Table of Contents

Experimental Section

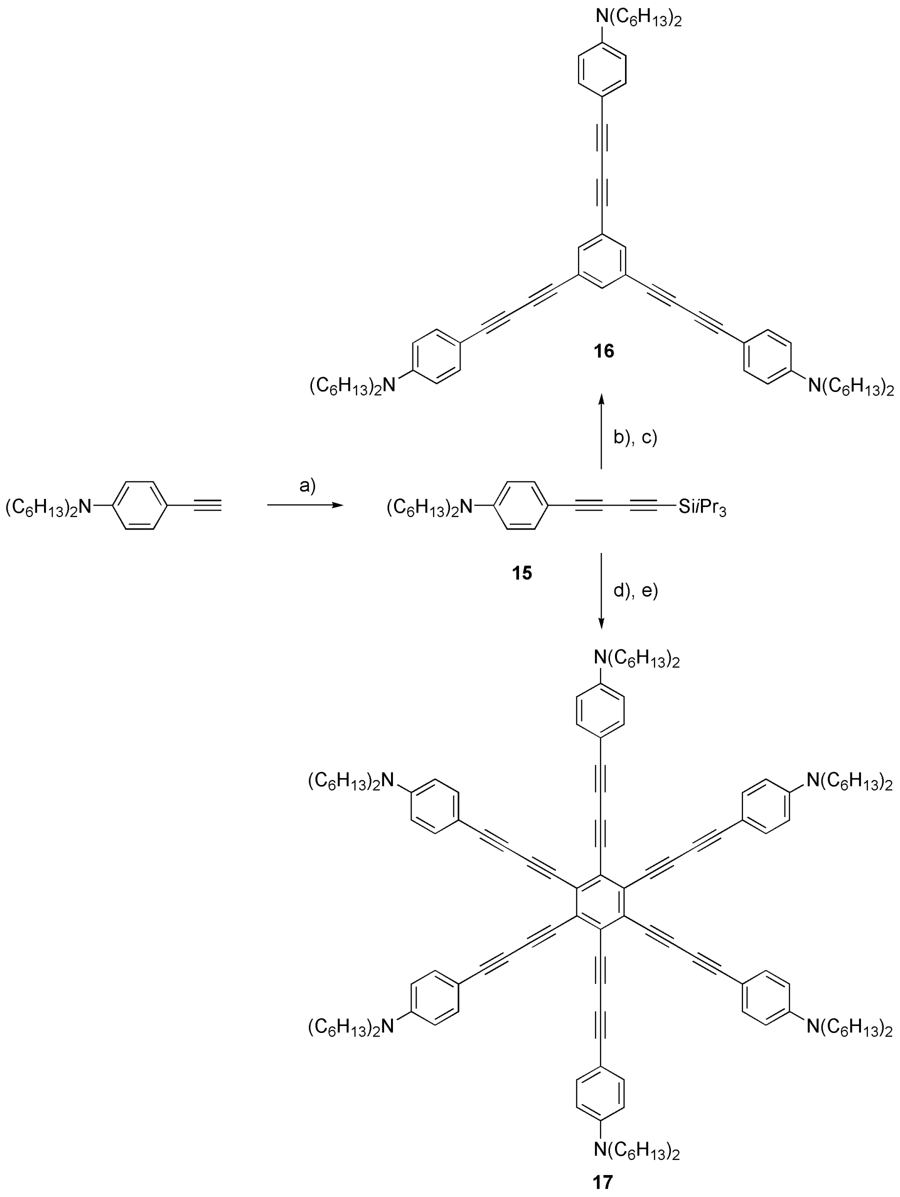
Materials and general methods: Reagents and solvents were purchased at reagent grade from Acros, Aldrich, and Fluka, and used as received. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone, and CH_2Cl_2 from CaH_2 under N_2. Hay catalyst refers to a freshly prepared solution of CuCl (100 mg, 1.0 mmol) and *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA; 0.15 mL, 1.0 mmol) in acetone (25 mL). All reactions, except Hay couplings, were performed under an inert atmosphere by applying a positive presure of N_2 or Ar. Column chromatography (CC) and plug filtrations were carried out with SiO_2 60 (particle size 0.040–0.063 mm, 230–400 mesh; Fluka) and distilled technical solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with SiO_2 60 F_{254} obtained from Macherey-Nagel; visualization with a UV lamp (254 or 366 nm). Melting points (m.p.) were measured on a Büchi B-540 melting-point apparatus in open capillaries and are uncorrected. "Decomp" refers to decomposition. ^1H NMR and ^{13}C NMR spectra were measured on a Varian Gemini 300 or on a Bruker DRX500 spectrometer at 20 °C unless otherwise stated. Chemical shifts (δ) are reported in ppm relative to the signal of tetramethylsilane (TMS). Residual solvent signals in the ^1H and ^{13}C NMR spectra were used as an internal reference. Coupling constants (*J*) are given in Hz. The apparent resonance multiplicity is described as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), sept (septuplet), and m (multiplet). Infrared spectra (IR) were recorded on a Perkin-Elmer FT1600; signal designations: s (strong), m (medium), w (weak). UV/Vis spectra were recorded on a Varian Cary-5 spectrophotometer. The spectra were measured in CH_2Cl_2 in a quartz cuvette (1 cm). The absorption wavelenghts (λ) are reported in nm with the extinction coefficient (ε) M^{-1} cm^{-1} in brackets; shoulders are indicated as sh. High-resolution (HR) EI-MS spectra were measured on a Hitachi-Perkin-Elmer VG-Tribrid spectrometer. HR FT-ICR-MALDI spectra were measured on an IonSpec Ultima Fourier transform (FT) instrument with [(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB), or 3-hydroxypicolinic acid (3-HPA) as matrix. The most important signals are reported in *m*/*z* units with *M* as the molecular ion. MALDI-TOF spectra were recorded on a Bruker Daltonics Ultraflex mass spectrometer using DCTB as matrix. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH Zürich, with a LECO CHN/900 instrument.

Electrochemistry: The electrochemical measurements were carried out at 20 °C in CH_2Cl_2, containing 0.1 M $n\mathrm{Bu_4NPF_6}$ in a classical three-electrode cell. CH_2Cl_2 was purchased in spectroscopic grade from Merck, dried over molecular sieves (4 Å), and stored under Ar prior to use. $n\mathrm{Bu_4NPF_6}$ 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 (0.1 to 10 V s^{-1}) or as rotating-disk electrode for rotating disk voltammetry (RDV). The auxiliary electrode was a platinum 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 ($\mathrm{Fc^+/Fc}$) couple, used as an internal standard, and are uncorrected from ohmic drop. The accessible range of potentials on the glassy carbon electrode was +1.4 to −2.4 V versus $\mathrm{Fc^+/Fc}$ in CH_2Cl_2. The cell was connected to a computerized multipurpose electrochemical device AUTOLAB (Eco

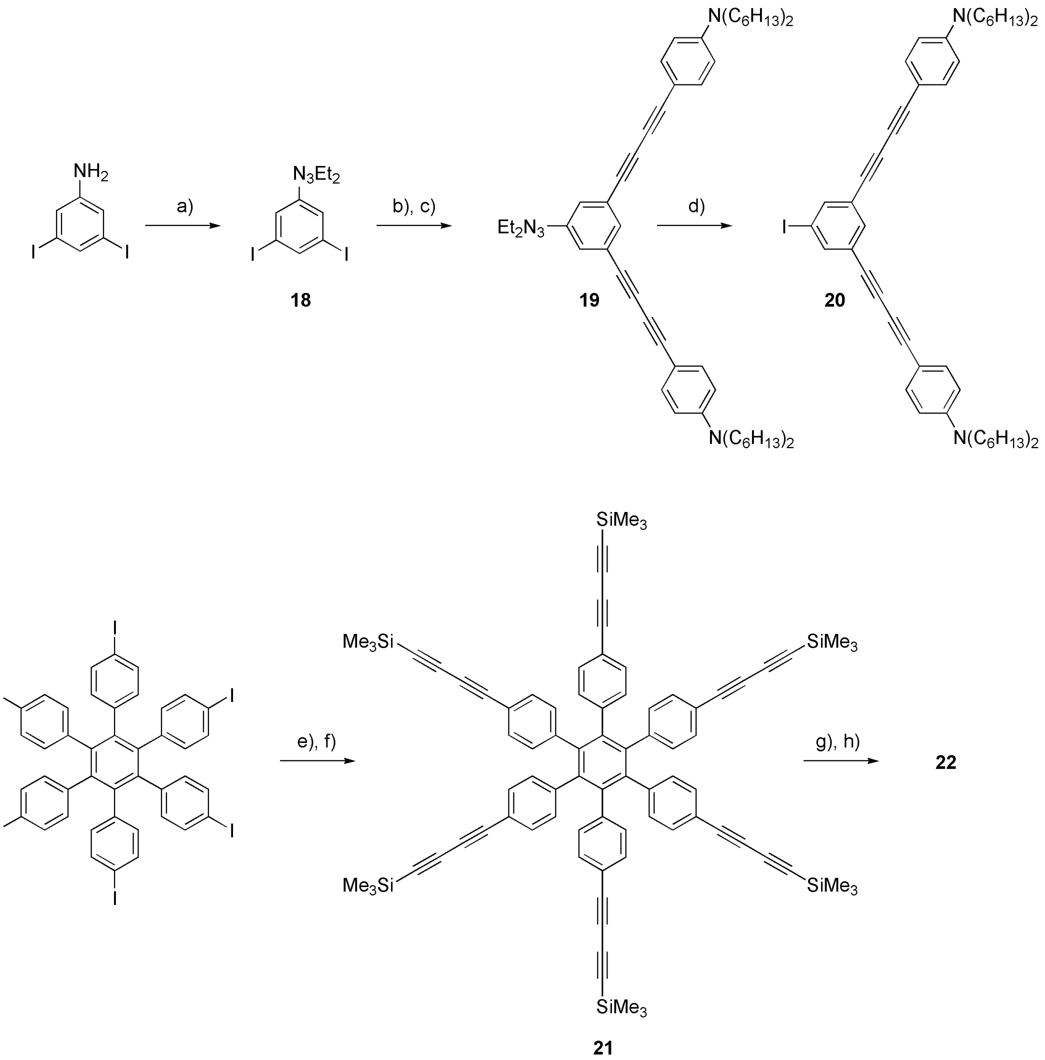
Chemie BV, Utrecht, The Netherlands) controlled by the GPSE software running on a personal computer. Simulations of the cyclic voltammetry were carried out using the DigiSim®3.0 software (Bioanalytical Systems Inc.).

X-ray structure of 7: Crystal data at 220(2) K for $C_{30}H_{20}N_6$, M_r = 464.52, monoclinic, space group $P2_1/c$ (no. 14), D_c = 1.225 g cm^{-3}, Z = 4, a = 7.5252(5), b = 8.4637(9), c = 39.5727(15) Å, β = 92.608(7)°, V = 2517.8(3) Å^3. Bruker-Nonius Kappa-CCD diffractometer, MoK$_\alpha$ radiation, λ = 0.7107 Å, μ = 0.075 mm^{-1}. A black crystal of **7** (linear dimensions ca. 0.15 × 0.13 × 0.05 mm) was obtained by slow diffusion of hexane into a solution of **7** in CH_2Cl_2. Numbers of measured and unique reflections are 7722 and 4559, respectively. (R_{int} = 0.054). The structure was solved by direct methods (SIRS-97)[1] and refined by full-matrix least-squares analysis (SHELXL-97),[2] using an isotropic extinction correction. All non H-atoms were refined anisotropically; H-atoms were refined isotropically, whereby H-positions are based on stereochemical considerations. Final $R(F)$ = 0.074, $wR(F^2)$ = 0.145 for 330 parameters and 2652 reflections with $I > 2\sigma(I)$ and $2.94 < \theta < 25.37°$(corresponding R-values based on all 4559 reflections are 0.139 and 0.172, respectively).

CCDC-644153 (**7**) contains the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax:+44(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk), or via www.ccdc.cam.ac.uk/ data_request/cif.



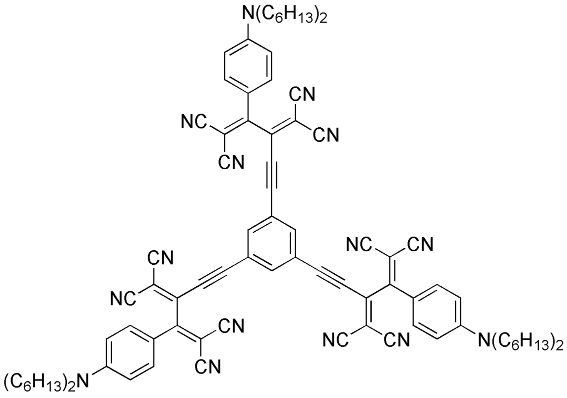
Scheme 1SI: Synthesis of the precursors **15**–**17**: a) (Triisopropylsilyl)acetylene, CuCl, TMEDA, air, acetone, 7 h, 20 °C, 64% (**15**). b) *n*Bu_4NF, THF, 30 min, 0 °C. c) 1,3,5-triiodobenzene, $[PdCl_2(PPh_3)_2]$, CuI, (*i*Pr)$_2$NH, 22 h, 60 °C, 83% (**16**) (yield over two steps). d) *n*Bu_4NF, THF, 20 min, 0 °C. e) hexaiodobenzene, {Pd[P(*o*-Tol)$_3$]$_2$}, CuI, NMP, Et_3N, 16 h, 60 °C, 6% (**17**) (yield over two steps). TMEDA = *N,N,N',N'*-tetramethylethylenediamine; THF = tetrahydrofurane, NMP = *N*-methylpyrrolidone.



Scheme 2SI: Synthesis of the dendritic precursor **22**: a) HCl, $NaNO_2$, Et_2O/THF/MeCN, 1.5 h, −5 °C, then K_2CO_3, Et_2NH, 3 h, 20 °C, 55% (**18**). b) **15**, *n*Bu_4NF, THF, 20 min, 0 °C. c) [$PdCl_2(PPh_3)_2$], CuI, (*i*Pr)$_2$NH, 14 h, 20 °C, 95% (**19**) (yield over two steps). d) NaI, Me_3SiCl, MeCN/CCl_4, 20 min, 60 °C, 50% (**20**). e) 1,4-Bis(trimethylsilyl)buta-1,3-diyne, MeLi·LiBr, THF, 3 h, 20 °C. f) Hexakis(4-iodophenyl)benzene, [$PdCl_2(PPh_3)_2$], CuI, (*i*Pr)$_2$NH, 14 h, 60 °C, 67% (**21**) (yield over two steps). g) *n*Bu_4NF, THF, 20 min, 0 °C. h) **20**, [$PdCl_2(PPh_3)_2$], CuI, (*i*Pr)$_2$NH, 14 h, 60 °C, 11% (**22**) (yield over two steps).

Synthetic Protocols:

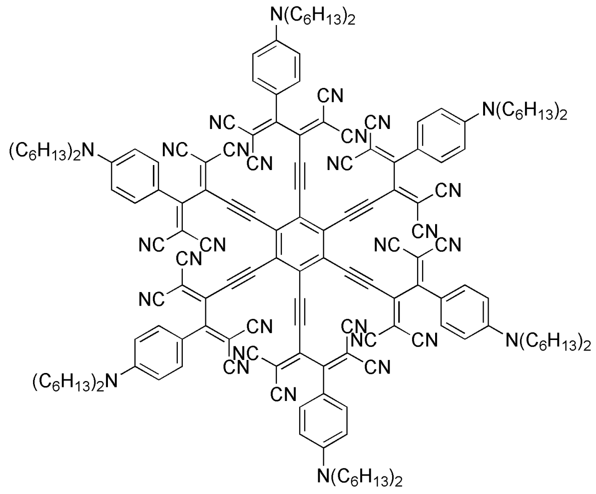
2,2'-[(5-{5,5-Dicyano-3-(dicyanomethylene)-4-[4-(dihexylamino)phenyl]pent-4-en-1-yn-1-yl}-1,3-phenylene)-diethyne-2,1-diyl]bis{3-[4-(dihexylamino)phenyl]buta-1,3-diene-1,1,4,4-tetracarbonitrile} (2)



A mixture of **16** (130 mg, 0.13 mmol) and TCNE (50 mg, 0.39 mmol) in CH_2Cl_2 (50 mL) was stirred for 10 h at 20 °C. The solvent was evaporated *in vacuo* and the residue subjected to CC (SiO_2, CH_2Cl_2/EtOAc 98:2) to give **2** (173 mg, 96%). Black metallic solid. R_f = 0.61 (SiO_2, CH_2Cl_2/EtOAc 98:2); M.p. 110-113 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (*t*, *J* = 6.7, 18 H), 1.33 (*s*, 36 H), 1.61 (*m*, 12 H), 3.40 (*t*, *J* = 7.8, 12 H), 6.70 (*d*, *J* = 9.4, 6 H), 7.76 (*d*, *J* = 9.4, 6 H), 7.93 ppm (*s*, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.18, 22.78, 26.82, 27.48, 31.68, 51.74, 72.27, 86.62, 97.37, 109.88, 111.13, 112.54, 113.82, 114.52, 116.48, 122.01, 132.88, 139.28, 150.33, 153.59, 157.88 ppm (21 out of 22 signals); IR (neat): $\tilde{\nu}$ = 2928m, 2857m, 2213m, 2188m, 1600s, 1534w, 1484s, 1445s, 1414s, 1345s, 1276m, 1213m, 1183s, 1118m, 978w, 888w, 819m cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 283 (47000), 363 (77700), 460 nm (114300); HR-MALDI-MS (3-HPA): *m*/*z*: 1384.7786 ([*M*H]$^+$, $C_{90}H_{94}N_{15}^+$, calc. 1384.7811);

Anal. calc. for $C_{90}H_{93}N_{15}$ (1384.83): C 78.06, H 6.77, N 15.17; found: C 78.35, H 6.93, N 15.09.

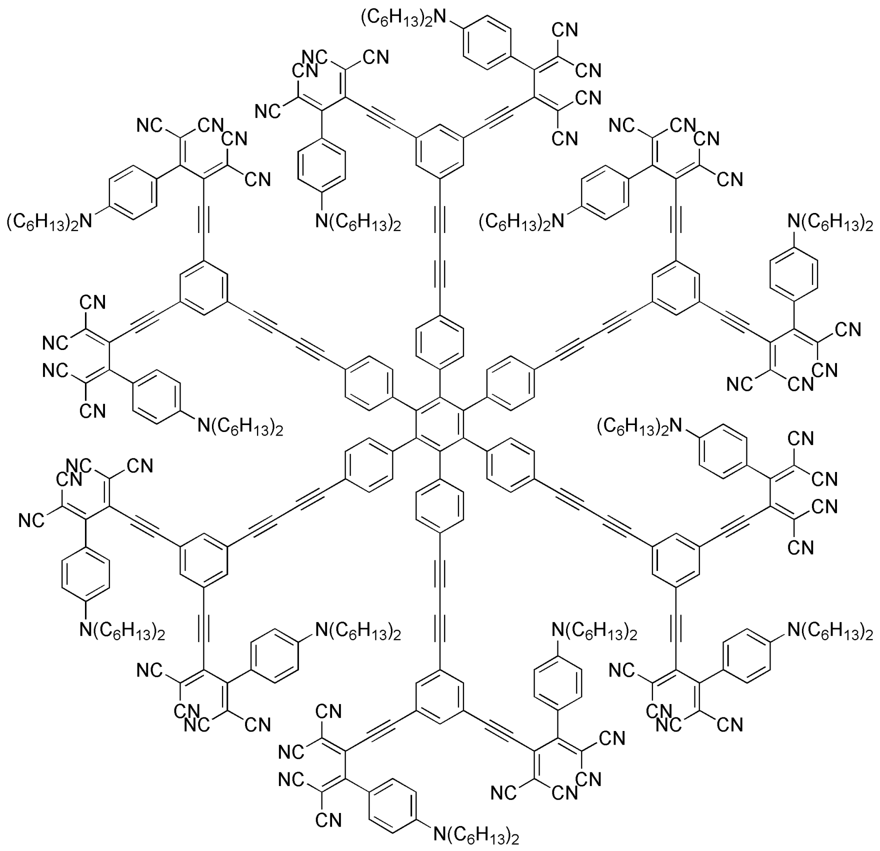
2,2',2'',2''',2''''-[(6-{5,5-Dicyano-3-(dicyanomethylene)-4-[4-(dihexylamino)phenyl]pent-4-en-1-yn-1-yl}benzene-1,2,3,4,5-pentayl)pentaethyne-2,1-diyl]pentakis{3-[4-(dihexylamino)phenyl]buta-1,3-diene-1,1,4,4-tetracarbonitrile} (3)



A mixture of **17** (4.2 mg, 2.2 μmol) and TCNE (1.7 mg, 13.1 μmol) in CH_2Cl_2 (5 mL) was stirred for 20 h at 20 °C. The solvent was evaporated *in vacuo* and the residue subjected to CC (SiO_2, CH_2Cl_2/EtOAc 30:1) to give **3** (4.5 mg, 77%). Black metallic solid. R_f = 0.83 (SiO_2, CH_2Cl_2/EtOAc 30:1); M.p. 121–123 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (*t*, *J* = 7.0, 36 H), 1.32 (*s*, 72 H), 1.62 (*m*, 24 H), 3.37 (*t*, *J* = 7.9, 24 H), 6.72 (*d*, *J* = 9.4, 12 H), 7.78 ppm (*d*, *J* = 9.4, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.98, 22.60, 26.67, 27.29, 31.48, 51.61, 71.62, 94.65, 99.10, 103.12, 109.35, 110.20, 112.60, 114.15, 114.46, 116.90, 128.34, 133.20, 148.68, 153.63, 155.92 ppm; IR (neat): $\tilde{\nu}$ = 2927m, 2856m, 2214m, 1601s, 1484s, 1446s, 1416s, 1343s, 1298m, 1257m, 1213s, 1184s, 1118m, 980w, 900w, 819m cm^{-}

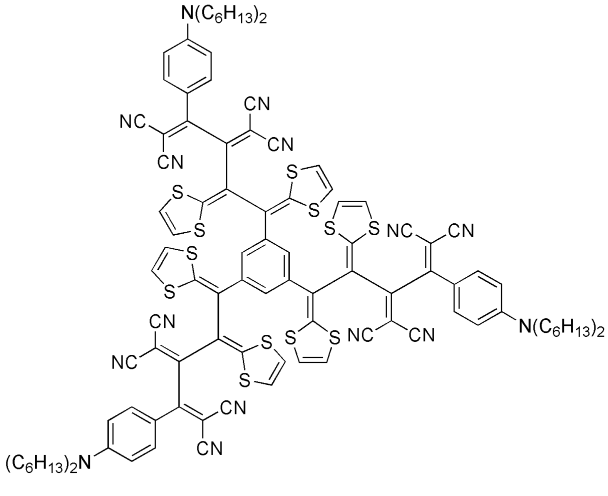
[1]; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (sh, 67600), 276 (68200), 396 (sh, 74800), 476 nm (110000); HR-MALDI-MS (3-HPA): *m*/*z*: 2690.5047 ([*M*H]$^+$, $C_{174}H_{180}N_{30}^+$, calc. 2690.5080).

3,3',3'',3''',3'''',3'''' ',3'''' '',3'''' ''',3'''' '''',3''' ' '''' ',3'''' '''' '',3'''' '''' '''-[Benzene-1,2,3,4,5,6-hexaylhexakis(1,4-phenylenebuta-1,3-diyne-4,1-diylbenzene-5,1,3-triyldiethyne-2,1-diyl)]dodecakis{2-[4-(dihexylamino)phenyl]buta-1,3-diene-1,1,4,4-tetracarbonitrile} (**4**)



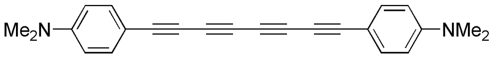
A mixture of **22** (2.5 mg, 0.50 µmol) and TCNE (1.3 mg, 10.1 µmol) in CH_2Cl_2 (3 mL) was stirred for 15 h at 20 °C. The solvent was evaporated *in vacuo* and the residue subjected to CC (SiO_2, CH_2Cl_2/EtOAc 98:2) to give **4** (2.8 mg, 86%). Black solid. R_f = 0.61 (SiO_2, CH_2Cl_2/EtOAc 98:2); M.p. 155–157 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (*t*, *J* = 6.9, 72 H), 1.31 (br *s*, 144 H), 1.61 (*m*, 48 H), 3.38 (*t*, *J* = 7.8, 48 H), 6.67 (*d*, *J* = 9.3, 24 H), 6.75 (*d*, *J* = 8.1, 12 H), 7.17 (*d*, *J* = 8.1, 12 H), 7.73 (*d*, *J* = 9.3, 24 H), 7.80 ppm (*s*, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.10, 22.64, 26.64, 27.31, 31.51, 51.53, 72.27, 73.42, 77.86, 83.52, 86.11, 96.61, 109.86, 111.06, 111.36, 112.32, 113.60, 114.40, 116.40, 118.93, 121.22, 124.68, 131.19, 131.70, 132.69, 136.45, 139.22, 139.81, 140.92, 144.21, 150.29, 153.38, 158.11 ppm; IR (neat): $\tilde{\nu}$ = 2923m, 2852m, 2213m, 2187m, 1601s, 1533w, 1485s, 1446s, 1414s, 1343s, 1291m, 1213m, 1182s, 1117m, 1018w, 980w, 884m, 819m cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 288 (68200), 306 (69700), 331 (sh, 83400), 357 (96300), 456 nm (91400); MALDI-TOF-MS (DCTB): *m*/*z*: 6507.20 ([*M*H]$^+$, $C_{438}H_{403}N_{60}^+$, calc. 6507.35).

2,2-[(5-{5,5-Dicyano-3-(dicyanomethylene)-4-[4-(dihexylamino)phenyl]-1,2-di-1,3-dithiol-2-ylidenepent-4-en-1-yl}-1,3-phenylene)bis(1,2-di-1,3-dithiol-2-ylideneethane-2,1-diyl)]bis{3-[4-(dihexylamino)phenyl]buta-1,3-diene-1,1,4,4-tetracarbonitrile} (**5**)



A mixture of **2** (40 mg, 0.03 mmol) and TTF (59 mg, 0.30 mmol) in MeCN (12 mL) was stirred under N_2 for 20 h at 60 °C. The solvent was evaporated *in vacuo* and the residue subjected to CC (SiO_2, $CH_2Cl_2 \rightarrow CH_2Cl_2$/EtOAc 95:5) to give **5** (27 mg, 47%). Black metallic solid. R_f = 0.35 (SiO_2, CH_2Cl_2/EtOAc 95:5); M.p. 214–217 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 353 K): δ = 0.86 (*t*, *J* = 6.7, 18 H), 1.26 (*s*, 36 H), 1.53 (*m*, 12 H), 3.20–3.34 (*m*, 12 H), 6.14 (*d*, *J* = 6.5, 2 H), 6.42 (*m*, 4 H), 6.66 (*m*, 8 H), 6.88–6.93 (*m*, 2 H), 7.02 (*s*, 2 H), 7.41 (*s*, 1 H), 7.67 (*s*, 2 H), 7.79–7.93 ppm (*m*, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$)[3]: δ = 14.02, 22.61, 26.70, 27.42, 31.59, 51.22, 51.37, 51.52, 69.76, 72.04, 73.81, 74.03, 112.37, 112.48, 114.18, 114.34, 115.28, 115.69, 116.07, 116.30, 116.47, 116.78, 118.39, 118.51, 119.04, 119.20, 119.35, 119.45, 119.79, 121.34, 122.13, 124.19, 127.47, 133.25, 133.48, 137.59, 138.83, 151.14, 151.27, 153.02, 153.28, 155.49, 155.74, 161.82, 162.60, 171.33, 173.89 ppm; IR (neat): $\tilde{\nu}$ = 3073w, 2921m, 2851m, 2203m, 1598s, 1489s, 1451s, 1413m, 1348m, 1287s, 1258m, 1209m, 1180s, 1102m, 983m, 948w, 932w, 888w, 820m, 804m cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 286 (sh, 45800), 385 (57600), 469 (sh, 130800), 482 nm (132000); HR-MALDI-MS (3-HPA): *m/z*: 1996.5346 ([*M*H]$^+$, $C_{108}H_{106}N_{15}S_{12}^+$, calc. 1996.5404).

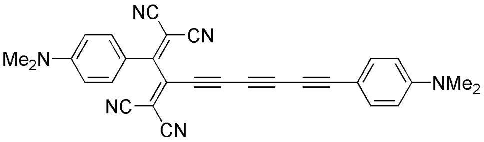
4,4'-Octa-1,3,5,7-tetrayne-1,8-diylbis(*N*,*N*-dimethylaniline) (**6**)



To a solution of *N*,*N*-dimethyl-4-[(triisopropylsilyl)buta-1,3-diyn-1-yl]aniline[4] (100 mg, 0.31 mmol) in THF (10 mL), *n*Bu_4NF

(1.0 M in THF, 0.62 mL) 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), and the solution was concentrated *in vacuo*. The residue was dissolved in acetone (5 mL). Hay catalyst (25 mL) was added, and the mixture was stirred while exposed to air for 3 h at 20 °C. The solvents were removed *in vacuo*, and the product was purified by CC (SiO_2, hexanes/CH_2Cl_2 1:1) to give **6** (82 mg, 79%). Orange solid. $R_f = 0.58$ (SiO_2, hexanes/CH_2Cl_2 1:1); M.p. 270 °C (decomp.); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): $\delta = 2.92$ (*s*, 12 H), 6.51 (*d*, $J = 9.0$, 4 H), 7.33 ppm (*d*, $J = 9.0$, 4 H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$): $\delta = 40.29$, 65.32, 67.95, 73.71, 80.79, 106.00, 111.93, 135.28, 151.21 ppm; IR (neat): $\tilde{\nu} = 2903$w, 2811w, 2180s, 2063m, 1596s, 1521m, 1436m, 1372s, 1296w, 1233m, 1188s, 1063m, 1012w, 978w, 946w, 805s cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 277 (31000), 286 (31200), 306 (33400), 328 (46600), 357 (sh, 54700), 379 (93200), 406 (83400), 444 nm (52700); HR-MALDI-MS (DCTB): *m*/*z*: 336.1626 ([*M*]$^+$, $C_{24}H_{20}N_2^+$, calc. 336.1621).

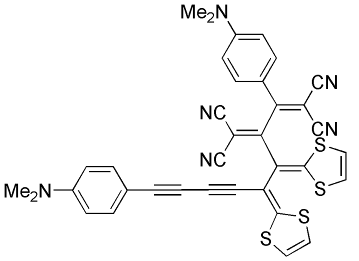
2-[4-Dimethylamino)phenyl]-3-{6-[4-(dimethylamino)phenyl]hexa-1,3,5-triyn-1-yl}buta-1,3-diene-1,1,4,4-tetracarbonitrile (7)



A mixture of tetrayne **6** (50 mg, 0.15 mmol) and TCNE (19 mg, 0.15 mmol) in CH_2Cl_2 (25 mL) was stirred for 10 h at 20 °C. The solvent was evaporated *in vacuo* and the residue subjected to CC (SiO_2, CH_2Cl_2) to give **7** (50 mg, 72%). Black metallic solid. $R_f = 0.45$ (SiO_2, CH_2Cl_2); M.p. 201 °C (**explosive**

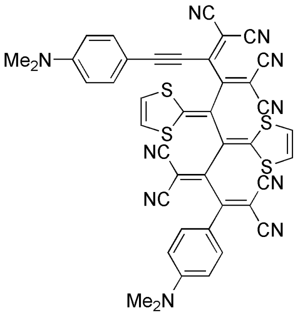
decomp.); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.05 (*s*, 6 H), 3.18 (*s*, 6 H), 6.60 (*d*, *J* = 9.0, 2 H), 6.73 (*d*, *J* = 9.0, 2 H), 7.43 (*d*, *J* = 9.0, 2 H), 7.73 ppm (*d*, *J* = 9.0, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.19, 40.41, 66.11, 72.80, 74.16, 74.24, 85.62, 92.89, 96.45, 102.36, 104.53, 110.49, 111.43, 111.86, 112.36, 113.41, 114.34, 117.31, 132.60, 135.60, 149.67, 151.99, 154.74, 159.45 ppm; IR (neat): $\tilde{\nu}$ = 2854w, 2212m, 2104s, 2051s, 1590s, 1527s, 1481s, 1436s, 1367s, 1336s, 1301m, 1265m, 1209m, 1169s, 1062m, 1012w, 990w, 941m, 901w, 813m cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 273 (47600), 338 (33900), 396 (sh, 44800), 443 (57700), 593 nm (36600); HR-MALDI-MS (3-HPA): *m*/*z*: 465.1825 ([*M*H]$^+$, $C_{30}H_{21}N_6^+$, calc. 465.1822); Anal. calc. for $C_{30}H_{20}N_6$ (464.53): C 77.57, H 4.34, N 18.09; found: C 77.80, H 4.50, N 17.80.

2-[4-Dimethylamino)phenyl]-3-{6-[4-(dimethylamino)phenyl]-1,2-di-1,3-dithiol-2-ylidenehexa-3,5-diyn-1-yl}buta-1,3-diene-1,1,4,4-tetracarbonitrile (**8**)



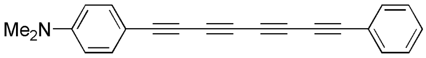
A mixture of **7** (20 mg, 0.04 mmol) and TTF (26 mg, 0.13 mmol) in MeCN (12 mL) was stirred under N_2 for 16 h at 60 °C. The solvent was evaporated *in vacuo* and the residue subjected to CC (SiO_2, CH_2Cl_2/EtOAc 95:5) to give **8** (23 mg, 80%). Deep red solid. R_f = 0.57 (SiO_2, CH_2Cl_2/EtOAc 95:5); M.p. 240 °C (decomp.); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 353 K): δ = 2.94 (*s*, 6 H), 3.08 (*s*, 6 H), 6.52 (*d*, *J* = 6.5, 1 H), 6.57 (*d*, *J* = 9.0, 2 H), 6.63 (*d*, *J* = 6.5, 1 H), 6.69 (*d*, *J* = 9.0, 2 H), 6.98 (*s*, 2 H), 7.34 (*d*, *J* = 9.0, 2 H), 7.85 ppm (*d*, *J* = 9.0, 2 H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$)[3]: δ = 40.34, 40.49, 71.93, 73.14, 73.51, 78.65, 83.20, 88.27, 99.40, 107.70, 107.95, 111.93, 112.66, 112.78, 114.04, 114.89, 115.92, 116.38, 116.67, 120.59, 121.63, 121.83, 125.26, 125.83, 128.31, 132.75, 132.94, 134.12, 135.96, 150.75, 155.09, 156.22, 162.14, 162.68, 165.04, 171.53 ppm; IR (neat): $\tilde{\nu}$ = 3094w, 3070w, 2917w, 2847w, 2801w, 2205m, 2114w, 1599s, 1521m, 1486m, 1457s, 1358s, 1212s, 1160s, 1024w, 981w, 943m, 902w, 860w, 807m cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 332 (41600), 397 (sh, 58000), 425 (69700), 481 nm (81500); HR-MALDI-MS (3-HPA): *m/z*: 707.0624 ([*M*+K]$^+$, $C_{36}H_{24}N_6S_4K^+$, calc. 707.0582), 691.0828 ([*M*+Na]$^+$, $C_{36}H_{24}N_6S_4Na^+$, calc. 691.0843), 669.1016 ([*M*H]$^+$, $C_{36}H_{25}N_6S_4^+$, calc. 669.1018).

3,6-Bis(dicyanomethylene)-2-[4-(dimethylamino)phenyl]-7-{[4-(dimethylamino)phenyl]ethynyl}-4,5-di-1,3-dithiol-2-ylideneocta-1,7-diene-1,1,8,8-tetracarbonitrile (9)



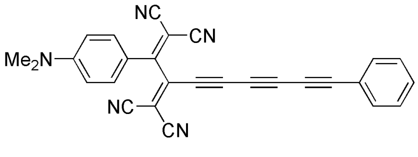
A mixture of **8** (8 mg, 12 μmol) and TCNE (1.5 mg, 12 μmol) in CH_2Cl_2 (6 mL) was stirred for 14 h at 20 °C. The solvent was evaporated *in vacuo* and the residue subjected to CC (SiO_2, CH_2Cl_2/EtOAc 95:5 → 92:8) to give **9** (8 mg, 83%). Black metallic solid. R_f = 0.33 (SiO_2, CH_2Cl_2/EtOAc 92:8); M.p. 245 °C (decomp.); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 353 K): δ = 3.07 (*s*, 6 H), 3.09 (*s*, 6 H), 6.61–6.72 (*m*, 4 H), 6.96 (*m*, 1 H), 7.03 (*s*, 2 H), 7.07 (*d*, *J* = 6.5, 1 H), 7.66–7.86 ppm (*m*, 4 H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$)[3]: δ = 40.42, 40.52, 40.60, 71.43, 72.49, 72.86, 73.60, 85.11, 86.39, 97.42, 98.89, 99.61, 100.38, 112.11, 112.46, 112.86, 113.47, 114.15, 114.82, 115.58, 115.65, 115.74, 115.93, 116.05, 116.93, 118.16, 118.76, 120.58, 120.83, 125.33, 125.45, 126.53, 126.78, 129.21, 132.53, 132.63, 133.09, 148.32, 154.64, 154.95, 155.25, 156.57, 160.44, 161.38, 173.26, 179.47 ppm; IR (neat): $\tilde{\nu}$ = 3083w, 2919w, 2863w, 2651w, 2207m, 2098s, 1601s, 1538w, 1481s, 1455m, 1367s, 1315s, 1284s, 1229m, 1211s, 1168s, 1122s, 1030m, 989m, 942m, 902w, 820m cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 289 (36000), 474 (110000), 551 nm (sh, 44700); HR-MALDI-MS (3-HPA): *m*/*z*: 835.0754 ($[M+K]^+$, $C_{42}H_{24}N_{10}S_4K^+$, calc. 835.0705), 819.0926 ($[M+Na]^+$, $C_{42}H_{24}N_{10}S_4Na^+$, calc. 819.0966), 797.1153 ($[MH]^+$, $C_{42}H_{25}N_{10}S_4^+$, calc. 797.1146).

***N*,*N*-Dimethyl-4-(8-phenylocta-1,3,5,7-tetrayn-1-yl)aniline (10)**



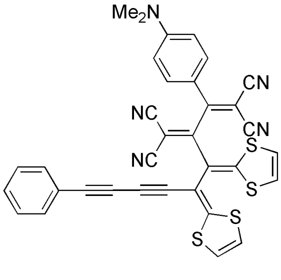
To a solution of *N*,*N*-dimethyl-4-[(triisopropylsilyl)buta-1,3-diyn-1-yl]aniline[4] (350 mg, 1.45 mmol) in THF (20 mL), *n*Bu_4NF (1.0 M in THF, 2.90 mL) was added. The mixture was stirred for 20 min at 0 °C, diluted with CH_2Cl_2, and filtered through a plug (SiO_2, CH_2Cl_2) and the solution was concentrated *in vacuo*. Simultaneously, 1-(trimethylsilyl)-4-phenyl-1,3-butadiyne[5] (58 mg, 0.29 mmol) in THF (8 mL) was treated with *n*Bu_4NF (1.0 M in THF, 0.58 mL) for 20 min at 0 °C. The mixture was diluted with CH_2Cl_2, filtered through a plug (SiO_2, CH_2Cl_2), and the solution was concentrated *in vacuo*. Both deprotected butadiynes were combined, dissolved in acetone (8 mL) and the resulting solution was added dropwise to Hay catalyst (25 mL). The mixture was stirred while exposed to air for 3 h at 20 °C. The solvents were removed *in vacuo*, and the product was purified by CC (SiO_2, hexanes/CH_2Cl_2 1:1) to give **10** (61 mg, 72%). Orange solid. $R_f = 0.67$ (SiO_2, hexanes/CH_2Cl_2 1:1); M.p. 156–157 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.02$ (*s*, 6 H), 6.59 (*d*, *J* = 9.0, 2 H), 7.33–7.43 (*m*, 5 H), 7.54 ppm (*d*, *J* = 9.0, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 40.19$, 63.76, 65.04, 67.21, 67.96, 73.45, 74.90, 77.72, 80.37, 106.06, 111.80, 121.00, 128.70, 129.98, 133.31, 134.99, 151.20 ppm; IR (neat): $\tilde{\nu} = 2897$w, 2806w, 2192s, 2161m, 2112s, 2066m, 1595s, 1526s, 1490m, 1441s, 1409m, 1370s, 1232m, 1198s, 1152s, 1066m, 1032w, 978m, 943m, 846w, 810s cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 268 (38000), 282 (49300), 310 (26500), 331 (24200), 351 (28400), 366 (sh, 21600), 396 (26600), 427 nm (21000); HR-MALDI-MS (DCTB): *m*/*z*: 293.1204 ([*M*]$^+$, $C_{22}H_{15}N^+$, calc. 293.1203).

2-[4-Dimethylamino)phenyl]-3-(6-phenylhexa-1,3,5-triyn-1-yl}buta-1,3-diene-1,1,4,4-tetracarbonitrile (**11**)



A mixture of tetrayne **10** (25 mg, 0.08 mmol) and TCNE (11 mg, 0.08 mmol) in CH_2Cl_2 (15 mL) was stirred for 14 h at 20 °C. The solvent was evaporated *in vacuo* and the residue subjected to CC (SiO_2, CH_2Cl_2) to give **11** (34 mg, 95%). Green metallic solid. R_f = 0.60 (SiO_2, CH_2Cl_2); M.p. 79–82 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 3.19 (*s*, 6 H), 6.75 (*d*, *J* = 9.3, 2 H), 7.38 (*t*, *J* = 7.4, 2 H), 7.48 (*t*, *J* = 7.3, 1 H), 7.57 (*d*, *J* = 7.2, 2 H), 7.72 ppm (*d*, *J* = 9.3, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.29, 64.42, 70.91, 73.68, 74.19, 82.07, 87.65, 98.07, 99.87, 109.82, 110.80, 112.15, 113.01, 113.91, 116.97, 119.32, 128.65, 131.03, 132.28, 133.33, 149.22, 154.42, 158.55 ppm; IR (neat): $\tilde{\nu}$ = 2919w, 2851w, 2213m, 2132s, 2090s, 1600s, 1533m, 1482s, 1435s, 1379s, 1334s, 1300s, 1260m, 1210s, 1170s, 1097s, 1063m, 1025w, 1002w, 899w, 820m cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 284 (47600), 300 (sh, 44300), 320 (sh, 33800), 370 (21600), 449 nm (55000); HR-MALDI-MS (3-HPA): *m*/*z*: 423.1484 ([*M*H]$^+$, $C_{28}H_{16}N_5^+$, calc. 423.1478).

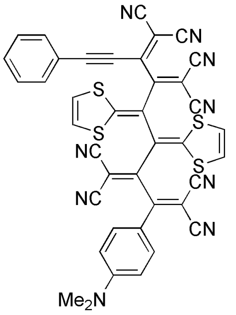
2-(1,2-Di-1,3-dithiol-2-ylidene-6-phenylhexa-3,5-diyn-1-yl)-3-[4-(dimethylamino)phenyl]buta-1,3-diene-1,1,4,4-tetracarbonitrile (12)



A mixture of **11** (20 mg, 0.05 mmol) and TTF (29 mg, 0.14 mmol) in MeCN (12 mL) was stirred under nitrogen for 17 h at 60 °C. The solvent was evaporated *in vacuo* and the residue subjected to CC (SiO_2, CH_2Cl_2/EtOAc 95:5) to give **12** (23 mg, 78%). Deep red solid. R_f = 0.53 (SiO_2, CH_2Cl_2/EtOAc 95:5); M.p. 253 °C (decomp.); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 353 K): δ = 3.08 (*s*, 6 H), 6.55 (*d*, *J* = 6.5, 1 H), 6.60–6.72 (*m*, 3 H), 6.99 (*s*, 2 H), 7.29 (m, 3 H), 7.48 (m, 2 H), 7.85 ppm (*d*, *J* = 9.2, 2 H); ^{13}C

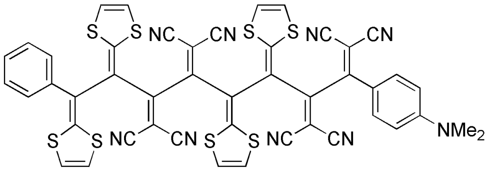
NMR (125 MHz, $C_2D_2Cl_4$)[3]: δ = 40.48, 40.50, 71.97, 73.59, 74.94, 78.36, 79.52, 82.38, 83.30, 86.25, 86.34, 98.66, 100.88, 112.63, 112.78, 114.03, 114.48, 114.88, 115.87, 116.30, 116.65, 120.32, 120.60, 121.86, 122.08, 125.24, 128.40, 128.75, 128.90, 129.50, 129.70, 132.61, 132.72, 132.93, 132.93, 154.96, 155.10, 156.26, 162.07, 164.20, 166.51, 171.73 ppm; IR (neat): $\tilde{\nu}$ = 3090m, 3074m, 2858w, 2205s, 2115m, 1601s, 1540w, 1470s, 1435m, 1385s, 1361s, 1287s, 1262m, 1212s, 1173s, 1076m, 1045m, 988w, 941m, 902w, 824m, 807m cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 285 (45600), 412 (67800), 480 nm (109900); HR-MALDI-MS (3-HPA): *m/z*: 664.0142 ($[M+K]^+$, $C_{34}H_{19}N_5S_4K^+$, calc. 664.0160), 648.0422 ($[M+Na]^+$, $C_{34}H_{19}N_5S_4Na^+$, calc. 648.0421), 626.0595 ($[MH]^+$, $C_{34}H_{20}N_5S_4^+$, calc. 626.0596).

3,6-Bis(dicyanomethylene)-2-[4-(dimethylamino)phenyl]-4,5-di-1,3-dithiol-2-ylidene-7-(phenylethynyl)octa-1,7-diene-1,1,8,8-tetracarbonitrile (13)



A mixture of **12** (8 mg, 13 µmol) and TCNE (3.3 mg, 26 µmol) in CH_2Cl_2 (6 mL) was stirred for 22 h at 20 °C. The solvent was evaporated *in vacuo* and the residue subjected to CC (SiO_2, CH_2Cl_2/EtOAc 95:5 → 92:8) to give **13** (9 mg, 92%). Black metallic solid. R_f = 0.23 (SiO_2, CH_2Cl_2/EtOAc 95:5); M.p. 237 °C (decomp.); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 353 K): δ = 3.09, 3.14 (*s*, 6 H), 6.74–6.88 (*m*, 2 H), 7.17 (*m*, 2 H), 7.35–7.53 (*m*, 5 H), 7.71–7.84 ppm (*m*, 4 H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): not available due to low solubility; IR (neat): $\tilde{\nu}$ = 3075w, 2920w, 2857w, 2651w, 2204s, 2171s, 1600s, 1488m, 1435s, 1333s, 1320s, 1208s, 1169s, 1121m, 1059m, 988m, 941m, 901w, 820m, 802w cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 279 (33800), 390 (53000), 465 nm (102100); HR-MALDI-MS (3-HPA): *m*/*z*: 776.0541 ([*M*+Na]$^+$, $C_{40}H_{19}N_9S_4Na^+$, calc. 776.0544), 754.0733 ([*M*H]$^+$, $C_{40}H_{20}N_9S_4^+$, calc. 754.0724).

3,6-Bis(dicyanomethylene)-2-(1,2-di-1,3-dithiol-2-ylidene-2-phenylethyl)-7-[4-(dimethylamino)phenyl]-4,5-di-1,3-dithiol-2-ylideneocta-1,7-diene-1,1,8,8-tetracarbonitrile (14)



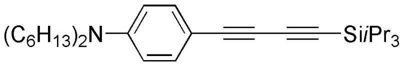
A) One-Pot Procedure

To a solution of tetrayne **10** (20 mg, 0.07 mmol) in CH_2Cl_2/MeCN (1:1, 16 mL), TCNE (44 mg, 0.34 mmol) and TTF (70 mg, 0.34 mmol) were added. The reaction mixture was stirred under N_2 for 22 h at 50 °C. The solvents were evaporated *in vacuo* and the residue subjected to CC (SiO_2, CH_2Cl_2 → CH_2Cl_2/EtOAc 95:5 → 80:20) to give **14** (14 mg, 21%). Black metallic solid. R_f = 0.20 (SiO_2, CH_2Cl_2/EtOAc 90:10); M.p. 260 °C (decomp.); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 353 K): δ = 3.12, 3.14 (*s*, 6 H), 6.28–6.43 (*m*, 3 H), 6.52–6.59 (*m*, 1 H), 6.71–6.76 (*m*, 2 H), 7.08–7.28 (*m*, 7 H), 7.77 (*m*, 2 H), 7.93 ppm (*m*, 2 H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): not available due to low solubility; IR (neat): $\tilde{\nu}$ = 3065m, 2920m, 2852m, 2692w, 2651w, 2198s, 1667m, 1601s, 1485m, 1434s, 1323s, 1209m, 1171m, 1086m, 1057m, 999m, 945m, 885m, 819m cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 287 (25900), 313 (sh, 23600), 462 nm (62100); HR-MALDI-MS (3-HPA): *m*/*z*: 995.9556 ([*M*+K]$^+$, $C_{46}H_{23}N_9S_8K^+$, calc. 995.9479), 979.9765 ([*M*+Na]$^+$, $C_{46}H_{23}N_9S_8Na^+$, calc. 979.9740), 957.9916 ([*M*H]$^+$, $C_{46}H_{24}N_9S_8^+$, calc. 957.9920).

B) Stepwise Procedure

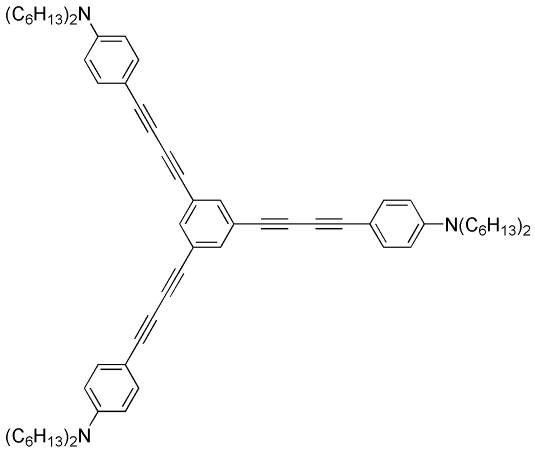
A mixture of **13** (4.9 mg, 6.5 μmol) and TTF (4.0 mg, 19.5 μmol) in CH_2Cl_2/MeCN (1:1, 4 mL) was stirred under N_2 for 3 h at 50 °C (prolonged reaction time led to an extensive decomposition). The solvent was evaporated *in vacuo* and the residue subjected to CC (SiO_2, CH_2Cl_2 → CH_2Cl_2/EtOAc 95:5 → 90:10) to give **14** (1.3 mg, 21%). Black metallic solid. Anal. data identical to those reported for **14** obtained by procedure **A**.

***N*,*N*-Dihexyl-4-[(triisopropylsilyl)buta-1,3-diyn-1-yl]aniline (15)**



To 4-ethynyl-*N*,*N*-dihexylaniline[6] (3.53 g, 12.4 mmol) and (triisopropylsilyl)acetylene (11.3 g, 61.8 mmol), Hay catalyst (750 mL) was added. The mixture was stirred for 7 h at 20 °C, filtered through a plug (SiO_2, acetone), and the solvent removed *in vacuo*. The residue was subjected to CC (SiO_2, hexanes/CH_2Cl_2 20:1) to yield **15** (3.70 g, 64%). Yellow oil. R_f = 0.30 (SiO_2, hexanes/CH_2Cl_2 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (*t*, *J* = 6.5, 6 H), 1.11 (*s*, 21 H), 1.32 (*s*, 12 H), 1.57 (*m*, 4 H), 3.26 (*t*, *J* = 7.6, 4 H), 6.51 (*d*, *J* = 9.0, 2 H), 7.34 ppm (*d*, *J* = 9.0, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.58, 14.22, 18.81, 22.87, 26.96, 27.33, 31.88, 51.11, 72.97, 77.88, 86.26, 90.75, 106.38, 111.21, 134.39, 148.69 ppm; IR (neat): $\tilde{\nu}$ = 2928m, 2863m, 2192m, 2097w, 1603s, 1519m, 1464w, 1404w, 1368w, 1295w, 1254w, 1189m, 996w, 883w, 812w cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 330 (sh, 35000), 349 nm (51600); HR-EI-MS (70 eV): *m*/*z* (%): 465.3784 (98, M^+, $C_{31}H_{51}NSi^+$; calc. 465.3791); Anal. calc. for $C_{31}H_{51}NSi$ (465.83): C 79.93, H 11.04, N 3.01; found: C 80.08, H 11.15, N 3.10.

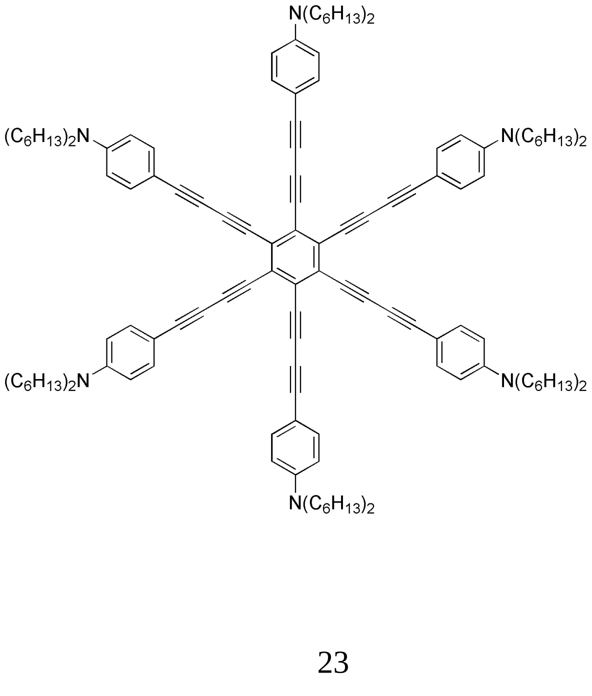
4,4',4''-(Benzene-1,3,5-triyltributa-1,3-diyne-4,1-diyl)tris(*N*,*N*-dihexylaniline) (**16**)



To a solution of **15** (690 mg, 1.48 mmol) in THF (20 mL), *n*Bu_4NF (1.0 M in THF, 4.4 mL) was added. The mixture was stirred for 30 min at 0 °C, diluted with CH_2Cl_2, and filtered through a plug (SiO_2, CH_2Cl_2), and the solvents were removed *in vacuo*. The residue was dissolved in diisopropylamine (50 mL), 1,3,5-triiodobenzene[7] (150 mg, 0.33 mmol) was added and the mixture deoxygenated thoroughly by bubbling N_2 through for 30 min. CuI (19 mg, 0.10 mmol) and [$PdCl_2(PPh_3)_2$] (46 mg, 0.07 mmol) were added, and the mixture was stirred under N_2 for 22 h at 60 °C. The mixture was diluted with CH_2Cl_2 and passed through a plug

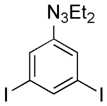
(SiO_2, CH_2Cl_2), and the solvents were removed *in vacuo*. The residue was subjected to CC (SiO_2, hexanes/CH_2Cl_2 4:1 → 2:1) to give **16** (272 mg, 83%). Yellow greasy solid. $R_f = 0.63$ (SiO_2, hexanes/CH_2Cl_2 4:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.92$ (*t*, $J = 6.5$, 18 H), 1.33 (*s*, 36 H), 1.59 (*m*, 12 H), 3.28 (*t*, $J = 7.6$, 12 H), 6.54 (*d*, $J = 9.0$, 6 H), 7.38 (*d*, $J = 9.0$, 6 H), 7.52 ppm (*s*, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.21$, 22.84, 26.91, 27.28, 31.83, 51.04, 71.77, 76.44, 78.72, 84.88, 106.07, 111.06, 123.47, 134.09, 135.25, 148.57 ppm; IR (neat): $\tilde{\nu} = 2952$m, 2924m, 2855m, 2204s, 2138w, 1598s, 1573m, 1517s, 1465m, 1413m, 1401m, 1365m, 1293w, 1254w, 1227w, 1195s, 1163m, 1107w, 1057w, 979w, 875w, 847w, 810s cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (48800), 272 (53300), 289 (57300), 309 (sh, 65000), 344 (102000), 370 (sh, 99000), 398 nm (130000); HR-MALDI-MS (3-HPA): *m*/*z*: 1000.7458 ([*M*H]$^+$, $C_{72}H_{94}N_3^+$, calc. 1000.7448).

4,4',4'',4''',4'''',4'''''-(Benzene-1,2,3,4,5,6-hexaylhexabuta-1,3-diyne-4,1-diyl)hexakis-(*N*,*N*-dihexylaniline) (17)[8,9]



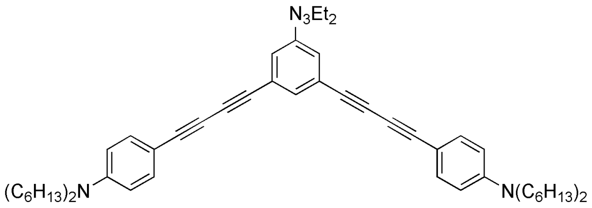
To a solution of **15** (558 mg, 1.20 mmol) in THF (20 mL), *n*Bu_4NF (1.0 M in THF, 3.6 mL) was added. The mixture was stirred for 20 min at 0 °C, diluted with CH_2Cl_2, and filtered through a plug (SiO_2, CH_2Cl_2), and the solvents were removed *in vacuo*. The residue was dissolved in triethylamine (2 mL) and the solution deoxygenated thoroughly by bubbling Ar through for 30 min. In a separate flask were placed hexaiodobenzene[10] (100 mg, 0.12 mmol), {Pd[P(*o*-Tol)$_3$]$_2$}[11] (13 mg, 0.02 mmol), CuI (11 mg, 0.06 mmol), anhydrous NMP (6 mL), and the mixture was deoxygenated thoroughly by bubbling Ar through for 30 min. To this mixture, the deprotected butadiyne solution in triethylamine was added and the reaction was stirred under Ar for 16 h at 60 °C. The mixture was diluted with CH_2Cl_2, and washed with H_2O (10 × 30 mL) and saturated aqueous NaCl solution (30 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Multiple CC (SiO_2, 3 × hexanes/CH_2Cl_2 4:1 → 2:1) afforded **17** (14 mg, 6%). Deep orange greasy solid. $R_f = 0.45$ (SiO_2, hexanes/CH_2Cl_2 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.88$ (*t*, *J* = 6.7, 36 H), 1.30 (*s*, 72 H), 1.51 (*m*, 24 H), 3.24 (*t*, *J* = 7.7, 24 H), 6.50 (*d*, *J* = 9.0, 12 H), 7.40 ppm (*d*, *J* = 9.0, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.00$, 22.68, 26.85, 27.19, 31.68, 50.97, 73.09, 77.33, 85.45, 88.23, 106.84, 111.09, 128.50, 134.34, 148.64 ppm; IR (neat): $\tilde{\nu}$ = 2950m, 2923m, 2854m, 2184s, 1598s, 1519s, 1465w, 1422m, 1401w, 1365m, 1294w, 1254w, 1227w, 1189s, 1106w, 1072m, 810s cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 284 (sh, 101300), 339 (288300), 354 (301700), 471 (243500), 495 nm (sh, 234900); HR-MALDI-MS (3-HPA): *m*/*z*: 1922.4250 ([*M*]$^+$, $C_{138}H_{180}N_6^+$, calc. 1922.4264).

1-(3,5-Diiodophenyl)-3,3-diethyltriaz-1-ene (18)



3,5-Diiodoaniline[7] (5.0 g, 14.5 mmol) was dissolved in a mixture of Et_2O/THF/MeCN 7:6:1 (100 mL), then conc. HCl (11 mL) was added and the solution cooled to −5 °C. A solution of $NaNO_2$ (3.4 g, 49.3 mmol) in MeCN/H_2O 2:3 (25 mL) was added slowly and the mixture stirred 1.5 h at −5 °C. The mixture was poured into a cold solution of K_2CO_3 (10.0 g , 72.5 mmol) and diethylamine (5.3 g, 7.5 mL, 72.5 mmol) in MeCN/H_2O 2:1 (150 mL). After stirring for 3 h at 20 °C, the mixture was extracted with CH_2Cl_2 (3 × 100 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by CC (SiO_2, hexanes/CH_2Cl_2 1:1 → 1:2) to yield triazene **18** (3.4 g, 55%) as a mixture of E/Z isomers. Brown oil. R_f = 0.83 (SiO_2, hexanes/CH_2Cl_2 1:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (br *s*, 6 H), 3.74 (*m*, 4 H), 7.72 (*d*, *J* = 1.5, 2 H), 7.75 ppm (*t*, *J* = 1.5, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.47 (br *s*), 14.77 (br *s*), 41.57 (br *s*), 49.49 (br *s*), 95.04, 129.14, 140.94, 153.47 ppm; IR (neat): $\tilde{\nu}$ = 2972w, 2931w, 1563m, 1535m, 1463m, 1445m, 1419m, 1388s, 1348s, 1335s, 1318s, 1281m, 1182m, 1114s, 1076s, 989m, 954m, 907m, 874m, 842s, 818w cm^{-1}; HR-EI-MS (70 eV): *m/z* (%): 428.9193 (22, M^+, $C_{10}H_{13}I_2N_3^+$; calc. 428.9199); Anal. calc. for $C_{10}H_{13}I_2N_3$ (429.04): C 27.99, H 3.05, N 9.79; found: C 28.04, H 3.03, N 9.74.

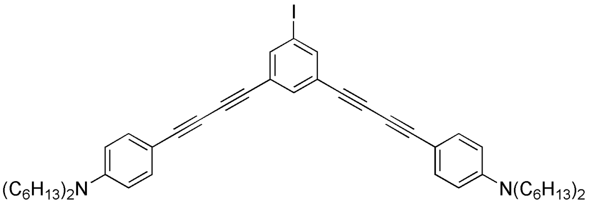
4,4'-({5-[3,3-Diethyltriaz-1-en-1-yl]-1,3-phenylene}dibuta-1,3-diyne-4,1-diyl)bis(*N*,*N*-dihexylaniline) (19)



To a solution of **15** (4.00 g, 8.59 mmol) in THF (100 mL), *n*Bu_4NF (1.0 M in THF, 25.8 mL) 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) and the solvents were removed *in vacuo*. The residue was dissolved in diisopropylamine (100 mL) and the solution deoxygenated thoroughly by bubbling Ar through for 30 min. Triazene **18** (1.50 g, 3.43 mmol), $[PdCl_2(PPh_3)_2]$ (480 mg, 0.69 mmol) and CuI (196 mg, 1.03 mmol) were added, and the mixture was stirred for 14 h at 20 °C. CH_2Cl_2 (400 mL) was then added and the mixture passed through a plug (SiO_2, CH_2Cl_2). The solvents were removed *in vacuo*, and the residue was purified by CC (SiO_2, hexanes/CH_2Cl_2 3:1 → 2:1) to give **19** (2.59 g, 95%). Yellow solid. M.p. 102–104 °C; R_f = 0.44 (SiO_2, hexanes/CH_2Cl_2 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (*t*, *J* = 6.4, 12 H), 1.32 (br *s*, 30 H), 1.57 (*m*, 8 H), 3.27 (*t*, *J* = 7.6, 8 H), 3.76 (*q*, *J* = 7.1, 4 H), 6.53 (*d*, *J* = 9.0, 4 H), 7.36 (*t*, *J* = 1.4, 1 H), 7.37 (*d*, *J* = 9.0, 4 H), 7.53 ppm (*d*, *J* = 1.4, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.24, 22.88, 26.97, 27.34, 31.88, 51.14, 72.11, 75.11, 80.38, 84.10, 106.66, 111.27, 123.29, 124.86, 132.12, 134.24, 148.73, 151.45 ppm (18 out of 20 signals); IR (neat): $\tilde{\nu}$ = 2925m, 2855m, 2205m, 2138w, 1598s, 1519s, 1464m, 1447m, 1399s, 1366s, 1349s, 1294m, 1253m, 1230m, 1188s, 1160m, 1107m, 1077w, 990w, 865w, 810s cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 273 (42400), 289 (53900), 307 (sh, 62200), 343 (103000), 357 (sh, 95000), 387 nm (101500); HR-MALDI-MS (DCTB): *m*/*z*: 791.5872 ([*M*]$^+$, $C_{54}H_{73}N_5^+$, calc. 791.5866);

Anal. calc. for $C_{54}H_{73}N_5$ (792.20): C 81.87, H 9.29, N 8.84; found: C 82.14, H 9.41, N 9.72.

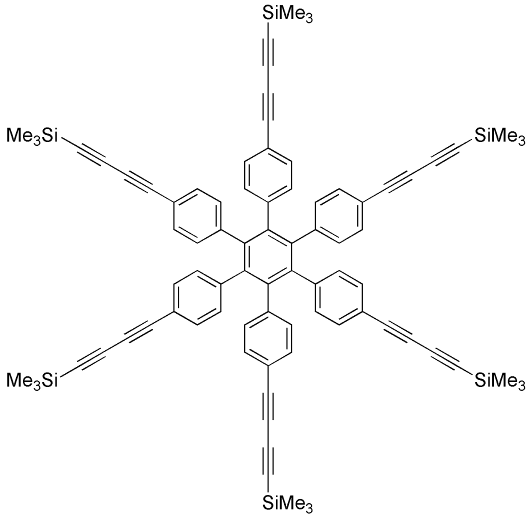
4,4'-[(5-Iodo-1,3-phenylene)dibuta-1,3-diyne-4,1-diyl]bis(*N*,*N*-dihexylaniline) (20)



To a solution of triazene **19** (500 mg, 0.63 mmol) in MeCN (30 mL) and CCl_4 (10 mL), NaI (331 mg, 2.21 mmol) and Me_3SiCl (205 mg, 250 µL, 1.89 mmol) were added. The mixture was stirred under N_2 at 60 °C for 20 min. Saturated aq. $NaHCO_3$ solution (20 mL) was added and the mixture extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvents removed in vacuo. The crude product was purified by CC (SiO_2, hexanes/CH_2Cl_2 4:1) to afford **20** (257 mg, 50%). Yellow viscous oil. R_f = 0.38 (SiO_2, hexanes/CH_2Cl_2 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (*t*, ***J*** = 6.2, 12 H), 1.32 (*s*, 24 H), 1.58 (*m*, 8 H), 3.28 (*t*, ***J*** = 7.6, 8 H), 6.54 (*d*, ***J*** = 9.0, 4 H), 7.37 (*d*, ***J*** = 9.0, 4 H), 7.53 (*s*, 1 H), 7.77 ppm (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.26, 22.89, 26.98, 27.34, 31.90, 51.15, 71.83, 78.13, 85.51, 93.27, 106.18, 111.29, 124.88, 134.36, 134.82, 140.70, 148.91 ppm (17 out of 18 signals); IR (neat): $\tilde{\nu}$ = 2950m, 2924m, 2854m, 2203s, 2138w, 1599s, 1576m, 1517s, 1464m, 1420m, 1401m, 1367m, 1294w, 1254w, 1196m, 1186m, 1164m, 1107w, 811m cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 271 (33400), 289 (33600), 310 (sh, 38000), 347 (66900), 371 (sh, 58000), 397 nm (71200); HR-MALDI-MS (3-

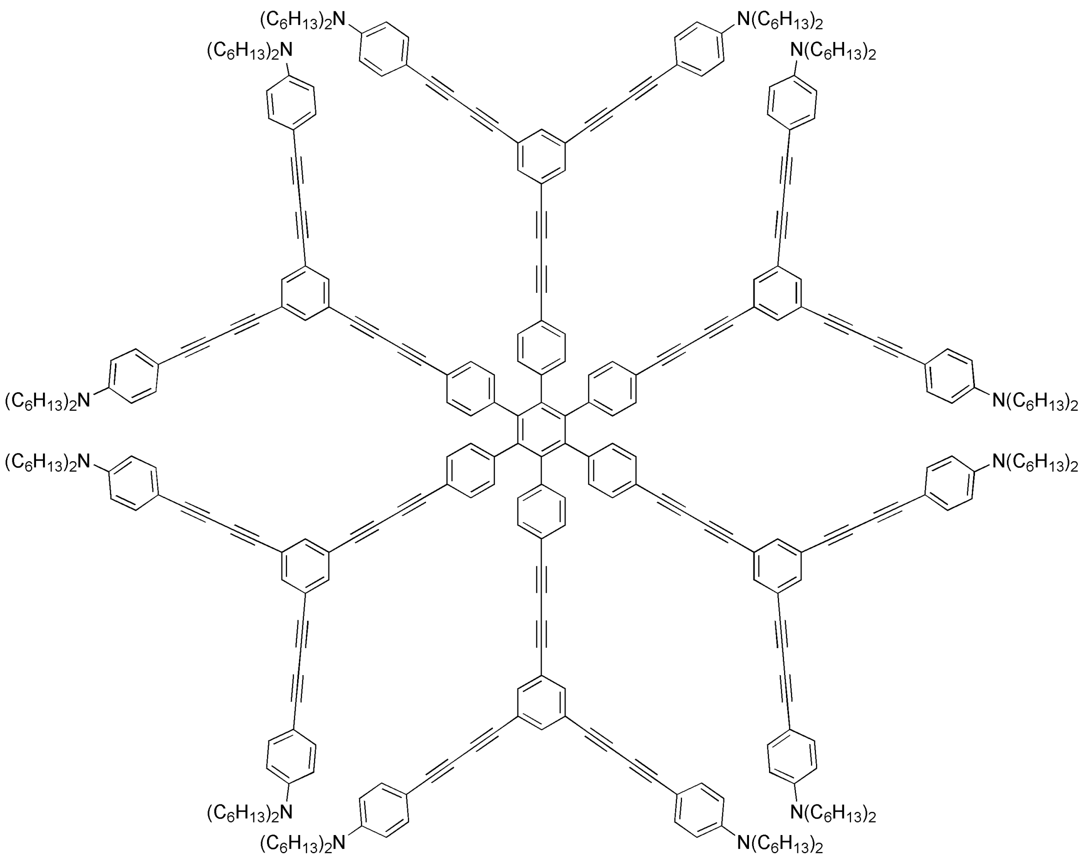
HPA): *m*/*z*: 819.4098 ([*M*H]$^+$, $C_{50}H_{64}IN_2^+$, calc. 819.4109); Anal. calc. for $C_{50}H_{63}IN_2$ (818.97): C 73.33, H 7.75, N 3.42; found: C 73.28, H 7.79, N 3.32.

Hexakis[4-(4-(trimethylsilyl)buta-1,3-diynyl)phenyl]benzene (21)



To a solution of 1,4-bis(trimethylsilyl)buta-1,3-diyne (180 mg, 0.93 mmol) in THF (10 mL), MeLi·LiBr (2.2 M in Et_2O, 0.42 mL, 0.93 mmol) was added and the mixture stirred for 3 h at 20 °C. Saturated aq. NH_4Cl solution (10 mL) was added and the mixture extracted with *n*pentane (3 × 20 mL). The combined organic layers were washed with saturated aq. NaCl solution (1 × 20 mL), dried ($MgSO_4$), and and concentrated *in vacuo* without heating to ca. 10% of the original volume. The residue was dissolved in diisopropylamine (10 mL), hexakis(4-iodophenyl)benzene[12] (80 mg, 0.062 mmol) was added and the mixture deoxygenated thoroughly by bubbling Ar through for 30 min. CuI (3.5 mg, 0.019 mmol) and $[PdCl_2(PPh_3)_2]$ (9 mg, 0.012 mmol) were added, and the mixture was stirred under Ar for 14 h at 60 °C. The mixture was concentrated *in vacuo* and the residue subjected to CC (SiO_2, hexanes/CH_2Cl_2 4:1 → 2:1) to give **21** (52 mg, 67%). Tan solid. M.p. 370 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.20 (*s*, 54 H), 6.66 (*d*, *J* = 8.1, 12 H), 7.00 ppm (*d*, *J* = 8.1, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.22, 74.72, 76.73, 88.02, 90.90, 119.23, 131.21, 131.70, 139.90, 140.67 ppm; IR (neat): $\tilde{\nu}$ = 2957w, 2894w, 2203w, 2103w, 1399w, 1249m, 1141w, 1106w, 1012m, 835s cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 274 (sh, 91600), 290 (159400), 310 nm (165200); HR-MALDI-TOF-MS (DCTB): *m*/*z*: 1254.489 ([*M*]$^+$, $C_{84}H_{78}Si_6^+$, calc. 1254.472).

4,4',4'',4''',4'''',4'''' ',4'''' '',4'''' ''',4'''' '''',4''' ' '''' ',4'''' '''' '',4'''' '''' '''-[Benzene-1,2,3,4,5,6-hexaylhexakis(1,4-phenylenebuta-1,3-diyne-4,1-diylbenzene-5,1,3-triyldibuta-1,3-diyne-4,1-diyl)]dodecakis(*N*,*N*-dihexylaniline) (**22**)



To a solution of **21** (10 mg, 8.0 μmol) in THF (5 mL), *n*Bu$_4$NF (1.0 M in THF, 0.10 mL) was added. The mixture was stirred for 20 min at 0 °C, diluted with CH_2Cl_2, filtered through a plug (SiO_2, CH_2Cl_2), and the solution was concentrated *in vacuo* to ca. 10% of the original volume. The residue was dissolved in diisopropylamine (10 mL), iodobenzene **20** (59 mg, 72 μmol) was added an the mixture deoxygenated thoroughly by bubbling Ar through for 30 min. CuI (4.0 mg, 22 μmol) and $[PdCl_2(PPh_3)_2]$ (10 mg, 14 μmol) were added, and the mixture was stirred under Ar for 14 h at 60 °C. The mixture was concentrated *in vacuo* and the residue subjected to CC (SiO_2, hexanes/CH_2Cl_2 5:1 → 2:1) to give **22** (4.3 mg, 11%). Yellow greasy solid. $R_f = 0.27$ (SiO_2, hexanes/CH_2Cl_2 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (*t*, *J* = 6.7, 72 H), 1.31 (br *s*, 144 H), 1.52 (*m*, 48 H), 3.25 (*t*, *J* = 7.7, 48 H), 6.51 (*d*, *J* = 9.0, 24 H), 6.76 (*d*, *J* = 8.0, 12 H), 7.11 (*d*, *J* = 8.0, 12 H), 7.35 (*d*, *J* = 9.0, 24 H), 7.53 ppm (*s*, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.01, 22.66, 26.77, 27.16, 31.67, 50.94, 71.74, 74.08, 75.27, 78.58, 79.56, 82.21, 84.86, 106.28, 111.14, 119.30, 122.89, 123.63, 131.16, 131.55, 134.15, 135.57, 136.38, 139.85, 140.67, 148.68 ppm (26 out of 27 signals); IR (neat): $\tilde{\nu}$ = 2923m, 2852m, 2203s, 2138w, 1598s, 1576s, 1517s, 1465m, 1401m, 1363s, 1293m, 1253m, 1226w, 1191s, 1164s, 1106w, 1058w, 1006w, 874m, 835m cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 262 (296100), 273 (322500), 289 (343700), 308 (405600), 328 (sh, 519000), 347 (588800), 395 nm (435300); MALDI-TOF-MS (DCTB): *m*/*z*: 4965.34 ([*M*]$^+$, $C_{366}H_{402}N_{12}^+$, calc. 4965.18).

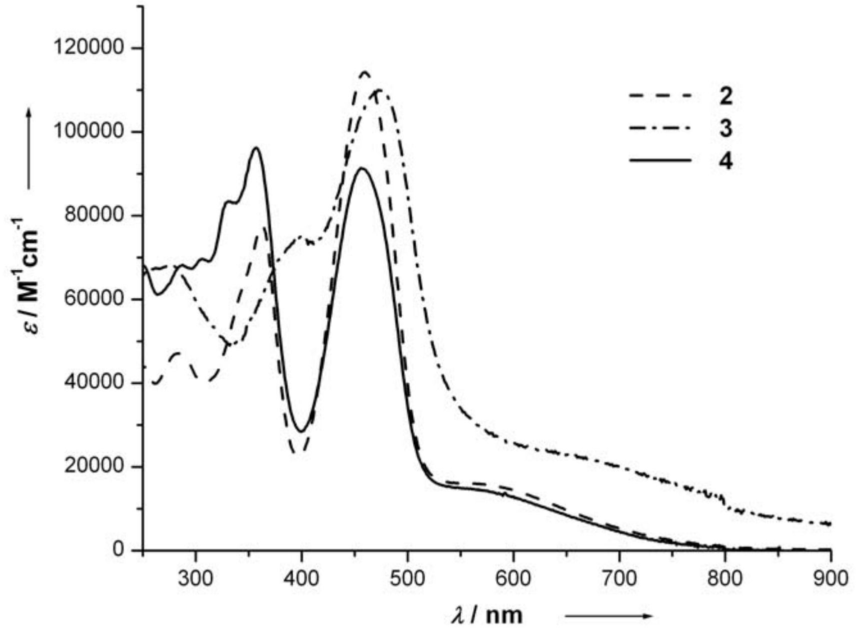


Figure 1SI: UV/Vis spectra of the multivalent CT chromophores **2**, **3**, and **4** in CH_2Cl_2.

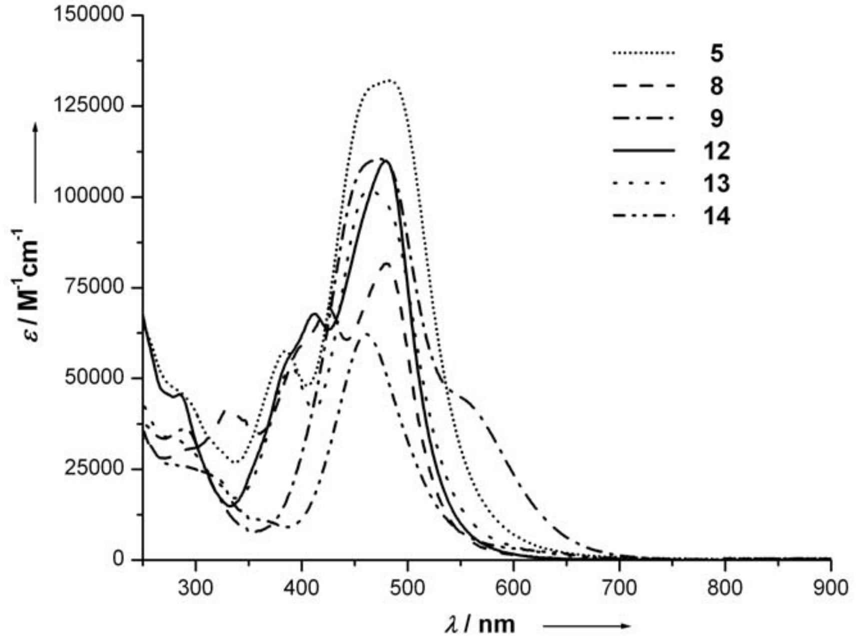


Figure 2SI: UV/Vis spectra of TCNE/TTF adducts **5**, **8**, **9**, and **12**–**14** in CH_2Cl_2.

Table 1SI. Electrochemical data of the TCNE/TTF adducts **7-14**. All potentials obtained by cyclic voltammetry (CV) and rotating disk voltammetry (RDV) in CH_2Cl_2 (+ 0.1 M *n*Bu$_4$NPF$_6$) are given *vs.* ferricinium/ferrocene (Fc^+/Fc) couple used as internal standard.

	Cyclic Voltammetry			Rotating Disk Voltammetry	
	$E°$ [V][a]	ΔE_p [mV][b]	E_p [V][c]	$E_{1/2}$ [V][d]	Slope [mV][e]
7			+0.86		
			+0.66	+0.65 (1e^-)	90
	−0.65	70		−0.66 (1e^-)	70
	−1.01	70		−1.06 (1e^-)	120
8			+0.73		
	+0.53	100		+0.53 (1e^-)	60
	+0.38	60		+0.36 (1e^-)	60
	−1.01	80		−1.07 (1e^-)	70
	−1.20	75		−1.27 (1e^-)	75
			−2.47		
9			+0.90		
	+0.70	75		+0.73 (2e^-)	40
	−0.85	90		−0.84 (1e^-)	60
				−1.06 (1e^-)	120
11	+0.93	90		+0.94 (1e^-)	70
	−0.60	100		−0.60 (1e^-)	70
	−0.98	110		−1.03 (1e^-)	90
12			+0.94		
	+0.55	75		+0.56 (2e^-)	40
	−1.10	110		−1.09 (1e^-)	80
			−1.28	−1.29 (1e^-)	100
			−2.78		
13			+1.03		
			+0.93	+0.90 (2e^-)	50
	−0.71	80		−0.73 (1e^-)	75

	−0.89	100		−0.94 (1e$^-$)	70
			−1.66		
14			+1.00	[f]	
			+0.73		
	+0.51	60			
	+0.43	90			
	−0.04	60			
			−1.10	−1.19	110
			−1.20		

[a] $E° = (E_{pc}+E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b] $\Delta E_p = E_{ox}-E_{red}$, where the subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively. [c] E_p = Irreversible peak potential. [d] $E_{1/2}$ = Half-wave potential. [e] Slope = Slope of the linearized plot of E versus $\log[I/(I_{lim}-I)]$, where I_{lim} is the limiting current and I the current. [f] Electrode inhibition during oxidation.

Discussion of the electrochemical results for the TCNE/TTF adducts 7-14.

The redox properties of D–A chromophores **7**–**9** and **11**–**14** were studied by CV and RDV. The compounds featuring one TCBD framework (**7**, **8**, **11**, and **12**) gave two reversible 1e$^-$ reductions (except for the second reduction of **12** that is irreversible). The presence of donating 1,2-di(1,3-dithiol-2-ylidene)ethane units shifts the reduction potential of the TCBD units to more negative potentials by 400 mV. Compound **8** is oxidized in two well separated 1e$^-$ steps (+0.36 V, +0.53 V) whereas **12** gives a single 2e$^-$ step (+0.56 V). This could be explained by the donating character of the additional *N*,*N*-dimethylamino group in **8**, shifting the first oxidation potential of the 1,2-di(1,3-dithiol-2-ylidene)ethane unit to more negative potentials. Chromophores **9** and **13** differ only by an additional *N*,*N*-dimethylamino substituent in **9**. As a result, the oxidation and reduction potentials are shifted in **9** to more negative potentials by about 150 mV in comparison to **13**. The proximity of two TCBD moieties in **9** and **13** results in an easier first reduction of the $C(CN)_2$ unit compared to **8** and **12**. The first oxidation of **14** occurs at a very low potential (−0.04 V), followed by two further oxidations. The other oxidations and reductions are not well resolved due to electrode inhibition. The steric crowding in **14** results in a twisted structure so that extended conjugation is no longer expected. Under these conditions, a discussion of the potentials is difficult.

Table 2SI: Electrochemical data of precursors **6**, **10**, **16**, **17**, and **22**. Observed by cyclic voltammetry (CV) and rotating disk voltammetry (RDV) in CH_2Cl_2 (+0.1 M $n\mathrm{Bu_4NPF_6}$). All potentials are given versus ferricinium/ferrocene (Fc^+/Fc) couple used as internal standard.

	Cyclic Voltammetry			Rotating Disk Voltammetry	
	$E°$ [V][a]	ΔE_p [mV][b]	E_p [V][c]	$E_{1/2}$ [V][d]	Slope [mV][e]
6			+0.52	[f]	
			−2.30		
10			+0.56	+0.54	60
			−2.20		
16			+0.54	+0.50	120
17			+0.51		
	−1.70	130		−1.55	120
22			+0.47	[f]	

[a] $E° = (E_{pc}+E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b] $\Delta E_p = E_{ox}-E_{red}$, where the subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively. [c] E_p = Irreversible peak potential. [d] $E_{1/2}$ = Half-wave potential. [e] Slope = Slope of the linearized plot of E versus $\log[I/(I_{lim}-I)]$, where I_{lim} is the limiting current and I the current. [f] Electrode inhibition during oxidation.

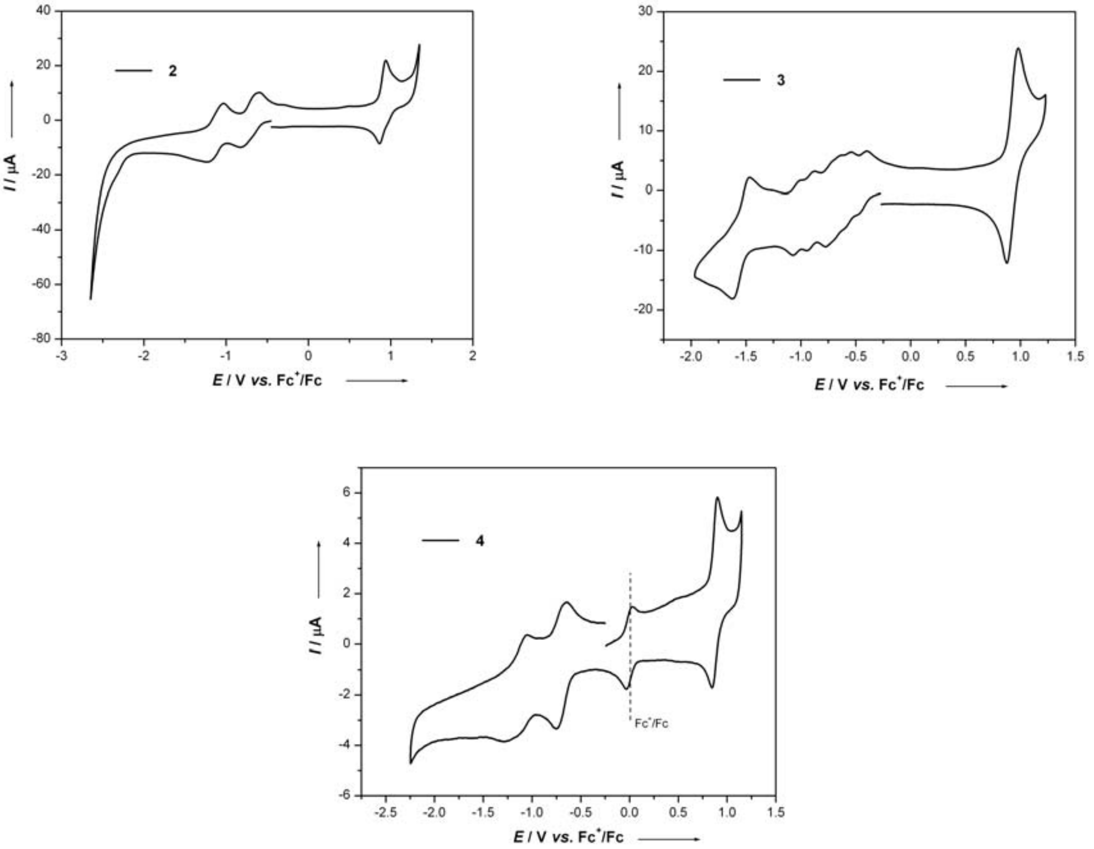


Figure 3SI: Cyclic voltammetry of **2**, **3**, and **4** on a glassy carbon working electrode in CH_2Cl_2 (+0.1 M nBu$_4$NPF$_6$) at scan rate v = 0.1 V s^{-1}.

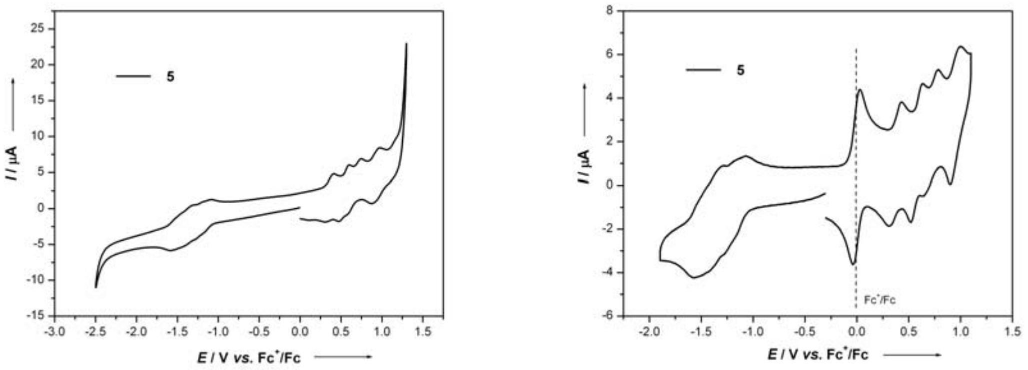


Figure 4SI: Cyclic voltammetry of **5** without and with ferrocene on a glassy carbon working electrode in CH_2Cl_2 (+0.1 M nBu$_4$NPF$_6$) at scan rate v = 0.1 V s^{-1}.

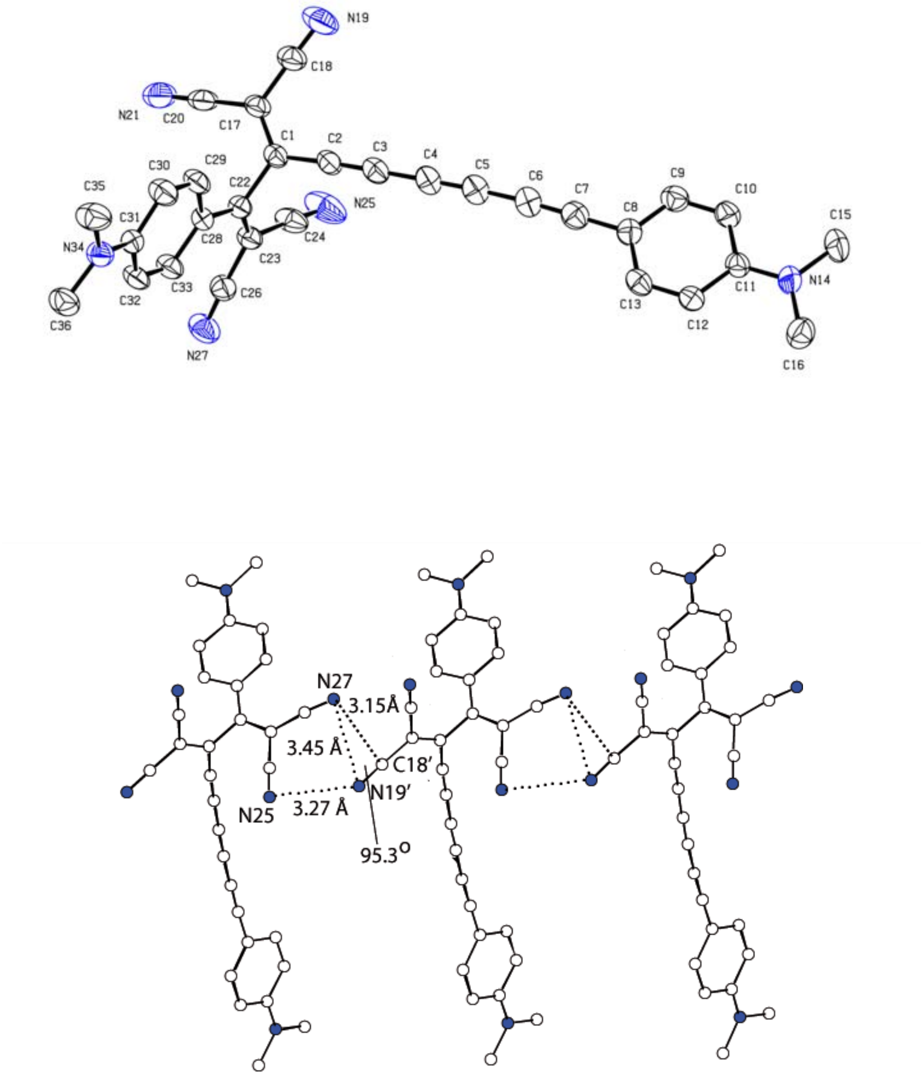


Figure 5SI: a) ORTEP plot of **7**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters at 220 K are drawn at the 30% probability level. Selected bond lengths [Å] and bond angles [°]: a) C(1)-C(2) 1.404(4), C(2)-C(3) 1.205(4), C(3)-C(4) 1.366(5), C(4)-C(5) 1.205(4), C(5)-C(6) 1.356(5), C(6)-C(7) 1.212(4), C(7)-C(8) 1.414(4), C(8)-C(9) 1.392(4), C(9)-C(10) 1.368(4), C(10)-C(11) 1.412(4), C(11)-C(12) 1.407(4), C(12)-C(13) 1.371(4), C(8)-C(13) 1.397(4), N(14)-C(11) 1.360(4), C(1)-C(17) 1.354(4), C(1)-C(22) 1.510(4), C(22)-C(28) 1.427(4), C(28)-C(29) 1.408(4), C(29)–C(30) 1.362(4), C(30)–C(31) 1.406(4), C(31)–C(32) 1.405(4), C(32)–C(33) 1.354(4), C(28)–C(33) 1.407(4), N(34)–C(31) 1.345(3), C(22)–C(23) 1.383(4); C(17)-C(1)-C(22) 121.0(3), C(23)-C(22)-C(1) 113.6(2), C(18)-C(17)-C(20) 117.8(3), C(26)-C(23)-C(24) 113.6(3). Selected torsion angles [°]: C(23)-C(22)-C(28)-C(33) = 2.7(5), C(36)-N(34)-C(31)-C(32) = –6.1(4). b) Arrangement of neighboring molecules in the crystal packing featuring favorable multipolar CN···CN interactions.

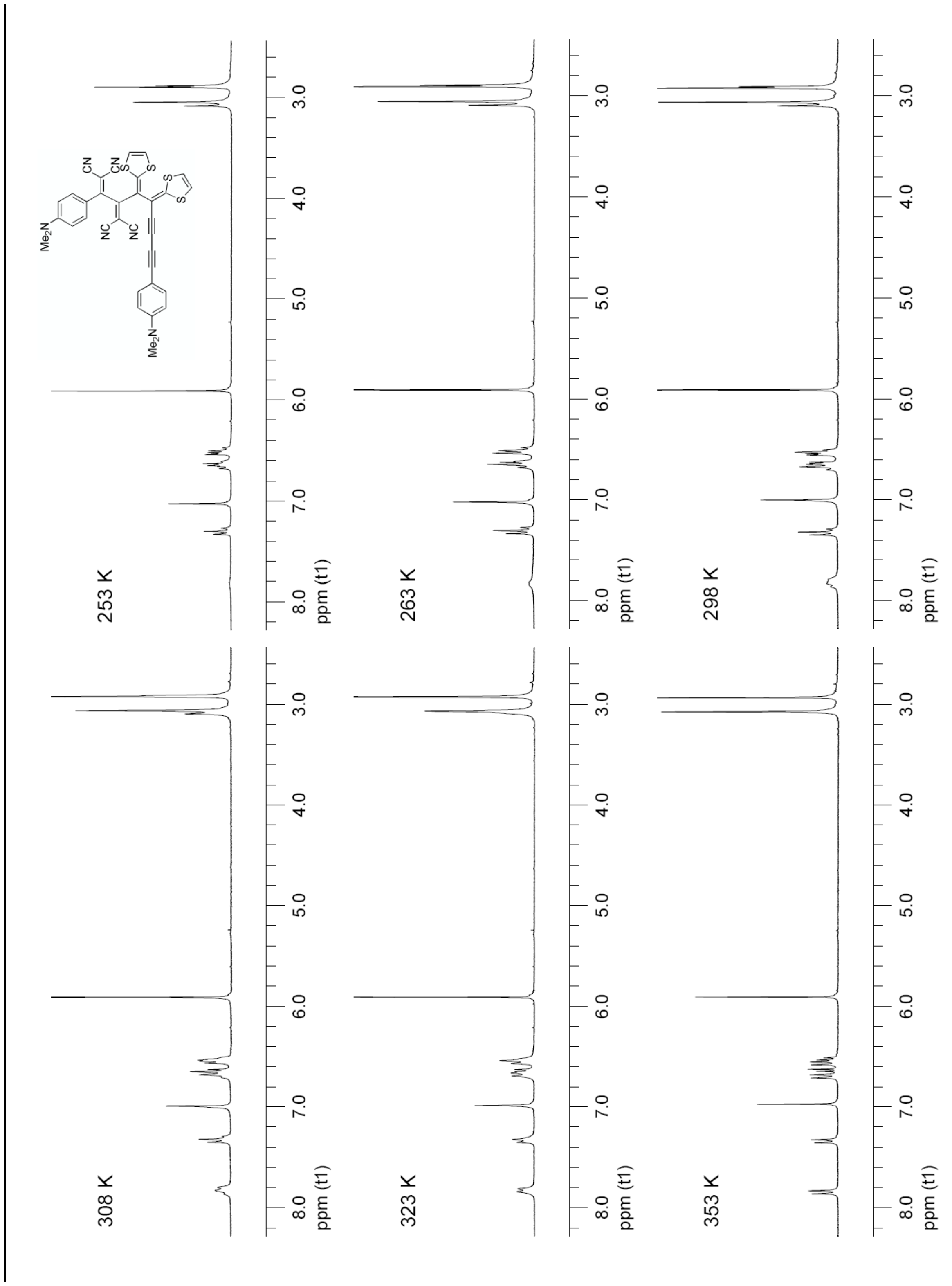


Figure 6SI: 300 MHz ^{1}H VT-NMR of **8** in $C_2D_2Cl_4$ showing the coalescence of signals, thus indicating the presence of a single constitutional isomer of **8** in solution.

References

[1] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115-119.

[2] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.

[3] Limited stability of chromophores **5**, **8**, **12**, **9**, **13**, and **14** at high temperatures together with their poor solubility at low temperatures reduced the available temperature range for VT-NMR experiments (253–353 K). Thus, only ^{1}H NMR spectra of derivatives **8** and **12** could be recorded even beyond the coalescence temperature of all signals. The temperature at which frozen conformations could be observed by ^{1}H NMR was not reached due to the low solubility of the compounds. The ^{13}C NMR coalescence was not observed within the available temperature range. Thus complex ^{13}C NMR spectra of **5**, **8**, **9**, and **12**–**14** are reported as empiric enumeration of observed signals.

[4] T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 1889–1905.

[5] V. Fiandanese, D. Bottalico, G. Marchese, A. Punzi, *Tetrahedron Lett.* **2003**, *44*, 9087–9090.

[6] F. Mitzel, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Helv. Chim. Acta* **2004**, *87*, 1130-1157.

[7] C. Willgerodt, E. Arnold, *Ber.* **1901**, *34*, 3343–3354.

[8] R. Boese, J. R. Green, J. Mittendorf, D. L. Mohler, K. P. C. Wollhardt, *Angew. Chem.* **1992**, *104*, 1643–1645; *Angew. Chem. Int. Ed.* **1992**, *31*, 1643–1645.

[9] W. B. Wan, M. M. Haley, *J. Org. Chem.* **2001**, *66*, 3893–3901.

[10] D. L. Mattern, *J. Org. Chem.* **1983**, *48*, 4772–4773.

[11] F. Paul, J. Patt, J. F. Hartwig, *Organometallics* **1995**, *14*, 3030–3039.

[12] K. Kobayashi, N. Kobayashi, M. Ikuta, B. Therrien, S. Sakamoto, K. Yamaguchi, *J. Org. Chem.* **2005**, *70*, 749–752.