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Oligoether-Substituted Derivatives of Carbon-Rich 1,4,7,10,13,16-Hexaethynyltribenzo[*a*,*e*,*i*]cyclododeca-5,11,17-triyne ($C_{36}H_{12}$) and 1,4,9,12-Tetrakis(ethynyl)dibenzo[*a*,*g*]cyclododeca-5,7,13,15-tetrayne ($C_{28}H_8$): Potential Precursors to the Circular [6]Phenylene ('Antikekulene') Frame

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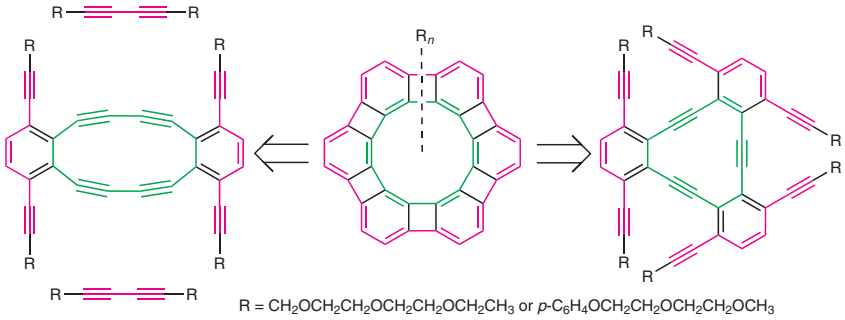

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Abstract The title compounds, in which the terminal alkyne functions are adorned with -$CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_3$ or -*p*-$C_6H_4OCH_2CH_2OCH_2CH_2OCH_3$ substituents, were synthesized. The strategies for their preparation relied on prior art and involved the use of Sonogashira alkynylations of appropriate haloarenes, Stephens–Castro cyclizations of 1,2,4-trialkynyl-3-iodobenzenes, and Hay oxidative couplings of 1,2,3,4-tetralkynylbenzenes. The targets form yellow materials, exhibiting yellow-green fluorescence, and they are very soluble in polar solvents, but only sparingly so in nonpolar media. Attempts to convert them into the antikekulene frame through $CpCo(CO)_2$-catalyzed (co)-cyclizations failed.

Key words alkynes, carbon-rich compounds, cyclotrimerizations, dehydroannulenes, phenylenes

Dehydrobenzannulenes ('benzocyclynes') have garnered significant attention, historically because of their ring current properties, but more recently because of their potential applications in material science, such as in optical electronic devices, nanomaterials, supramolecular constructs, 2D carbon nets, liquid crystals, as monomers in topochemical and other polymerizations, and more.[1] We have reported on the recognition that some such arrays, when suitably adorned by additional ethynyl substituents, for example **2**, could be related retrosynthetically to the first member of the circular phenylenes, circular [6]phenylene ('antikekulene') ([*N*] = number of benzene rings) **1**, by $CpCo(CO)_2$-catalyzed alkyne cyclotrimerization (Figure 1).[2,3] The phenylenes constitute a unique class of strained cyclohexatrienoid hydrocarbons in which benzene rings are fused to cyclobutadienes in an alternating manner.[4] In this series, the elusive circular members are special, because the bond fixation exerted by the antiaromatic four-membered rings enforces superdelocalization of the inside and outside 4n π electronic circuits.[2,3,5] Unfortunately, our attempts to effect the conversion of the sensitive oligoalkyne **2a** into the corresponding targets led only to decomposition. Introduction of stabilizing and solubilizing alkyl groups (as in **2b**,**c**) was helpful in as much as single and, more slowly, double cyclization could be accomplished. However, further progress was arrested, even under high temperature conditions, eventually leading only to disintegration of materials.[2a,3] In the present report, we describe our attempts to complete the circular frame of **1** by testing the oligoether bearing substrates **2d**,**e** in this strategy. During the course of these investigations, compounds that allowed the construction of **4a**,**b** became available, in turn permitting the examination of an as yet untested alternative approach to the target derivatives **3a**,**b** by cocyclization of the former with **5a**,**b** (Figure 1). Oligoether substituents of the type shown have been used advantageously in synthetic and materials applications of related systems.[1c–h,6,7] In our case, we hoped that they would address specifically our concerns of robustness and solubility of the final targets as well as their precursors, as well as possibly facilitate metal-catalyzed transformations by ligation. In a more general synthetic vein, these efforts would make available an array of new synthetic building blocks of potential utility to practitioners in the field.

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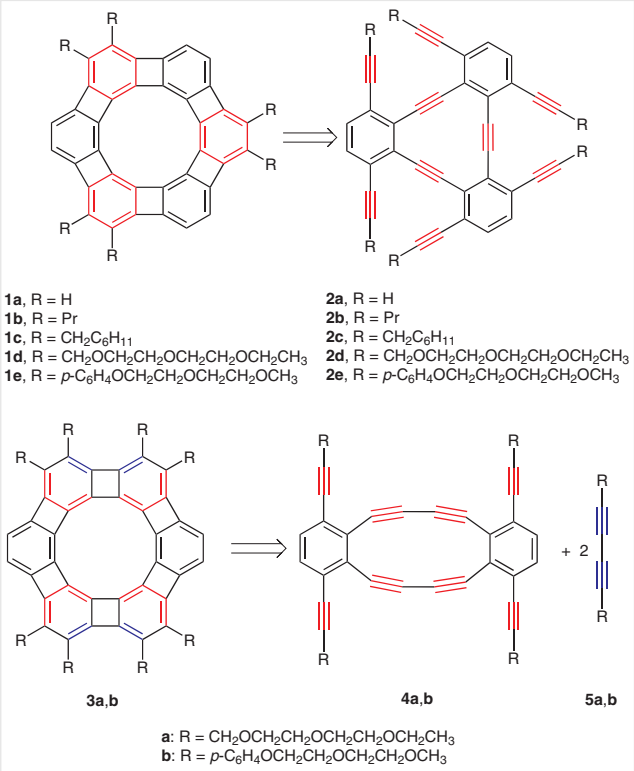
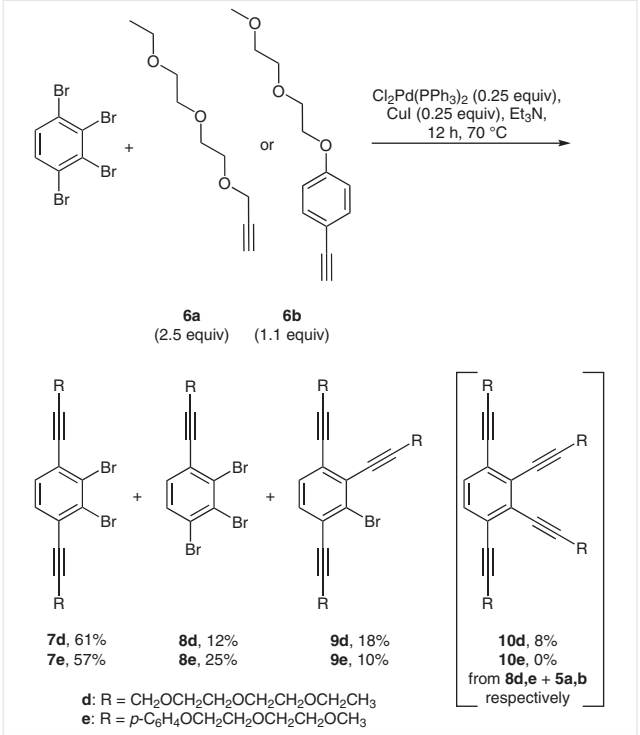


Figure 1 Retrosynthetic disconnection of the circular [6]phenylene frames **1** and **3** to the ethynylated benzocyclynes **2** and **4**, respectively



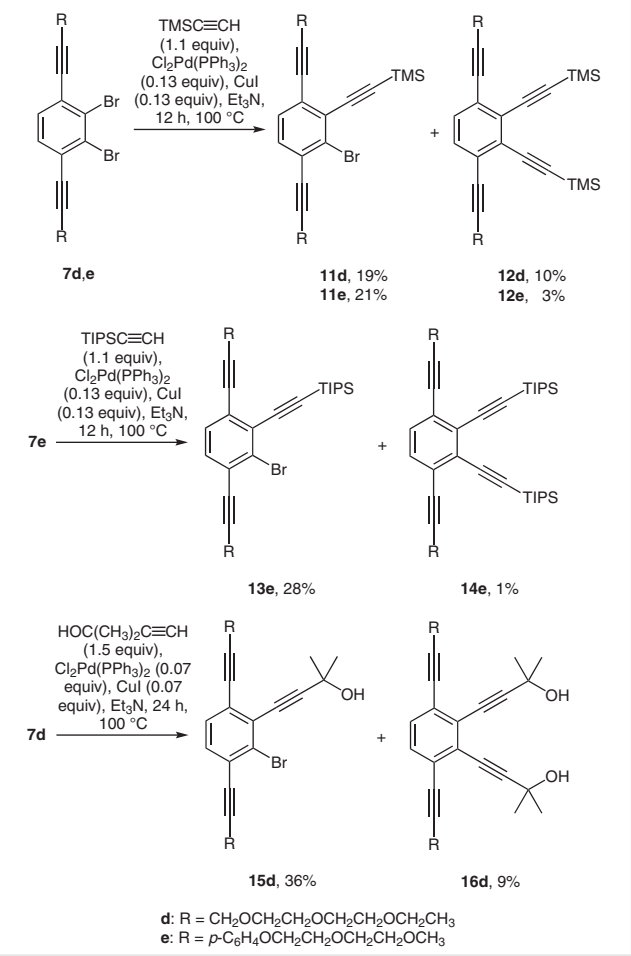
Scheme 1 Alkynylation of 1,2,3,4-tetrabromobenzene with **6a** and **6b**, respectively, to assemble **7d**,**e**–**9d**,**e**; tetraalkynyl derivative **10d** is generated during the alkynylation of **8d** with **6a**, in addition to **7d** and **9d**

The synthesis of **2d**,**e** relied on the respective strategies executed previously,[2a,3] but employing the oligoether alkynes **6a**[8] or **6b**[9] (see experimental section and SI) as the peripheral alkyne substituent synthons. The route to **2d**,**e** entailed in the first step the Pd-catalyzed 1,4-dialkynylation of 1,2,3,4-tetrabromobenzene[10] to **7d**,**e** (Scheme 1).[11]

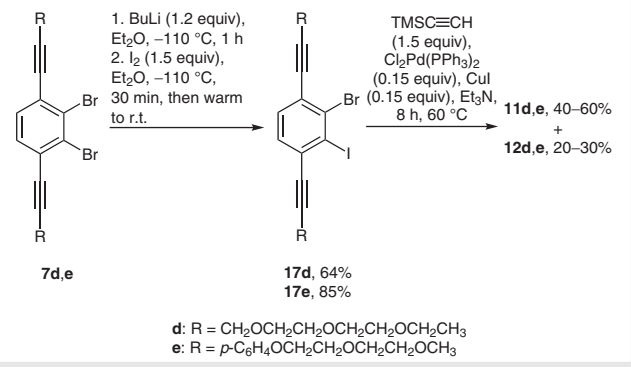
The desired products could be obtained in moderate yields, comparable to those acquired in the construction of **2b**,**c**,[2a] in addition to the under- and overalkynylated systems **8d**,**e** and **9d**,**e**, respectively. Reexposure of the former to the reaction conditions allowed for a significant improvement of the overall yield of **7** (**8d** → **7d**, 65%; **8e** → **7e**, 59%; see experimental section). In the case of **8d**, this process also generated small amounts of the tetrayne **10d**.

The next task was the introduction of a single (initially protected) ethynyl group to **7**, completing the composition of the basic building block that assembles **2** on cyclotrimerization (Scheme 2). Unfortunately, this step proved to be cumbersome. For example, treatment of **7d**,**e** with (trimethylsilyl)acetylene (1.1 equiv) at 100 °C generated the desired **11d**,**e** in only ~20% yield, in addition to the tetralkynyl systems **12d**,**e** and significant amounts of unreacted starting dibromide ~70%; see experimental section). The second alkynylation could not be suppressed under various reaction conditions, moreover **12** was difficult to separate from **11**, and attempts to push conversion of **7d**,**e** with excess (trimethylsilyl)acetylene and at temperatures >100 °C only increased the amounts of **12** formed. Similar problems were encountered in the assembly of **13e** and **15d**, respectively (Scheme 2). Thus, while switching to (triisopropylsilyl)acetylene (performed for only **7e**) served to reduce the amount of tetralkynyl product formed, conversion of dibromide remained poor (60% recovery). Turning to 2-methylbut-3-yn-2-ol (performed for only **7d**) improved the yield of monoalkynylation (to **15d**), but also that of **16d**, with 36% of **7d** remaining. Interest in alkyne **15d** stemmed from the hope that it might function as a direct precursor to **2d** by in situ deprotection and Pd-catalyzed cyclization, as reported for a preparation of the parent tribenzo[*a*,*e*,*i*]-cyclododeca-5,11,17-triyne.[12]

Unsatisfied by this state of affairs, it was thought that a more selective monoalkynylation might be attained by exchanging one of the bromines in **7d**,**e** with iodine. Indeed, low-temperature lithiation with BuLi, followed by exposure to I_2 resulted in fairly good yields of **17d**,**e** (Scheme 3).[13] However, again, further Pd-catalyzed coupling with (trimethylsilyl)acetylene, while proceeding more efficiently than that of **7d**,**e** (Scheme 2), still gave significant amounts of doubly coupled derivatives **12d**,**e** (Scheme 3), detracting from the synthetic utility of the sequence.

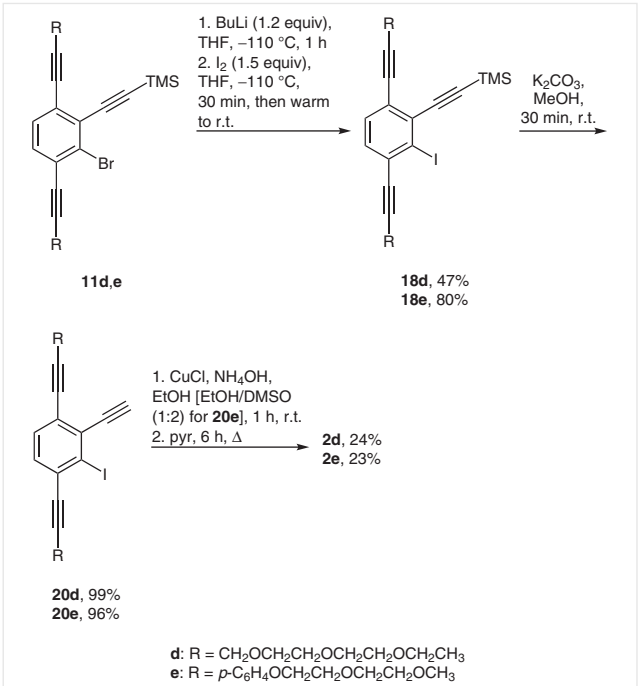


Scheme 2 Various monoalkynylations of **7d**,**e**



Scheme 3 Bromine–iodine exchange of **7d**,**e** to give **17d**,**e** and subsequent (trimethylsilyl)ethynylation to **11d**,**e** and **12d**,**e**

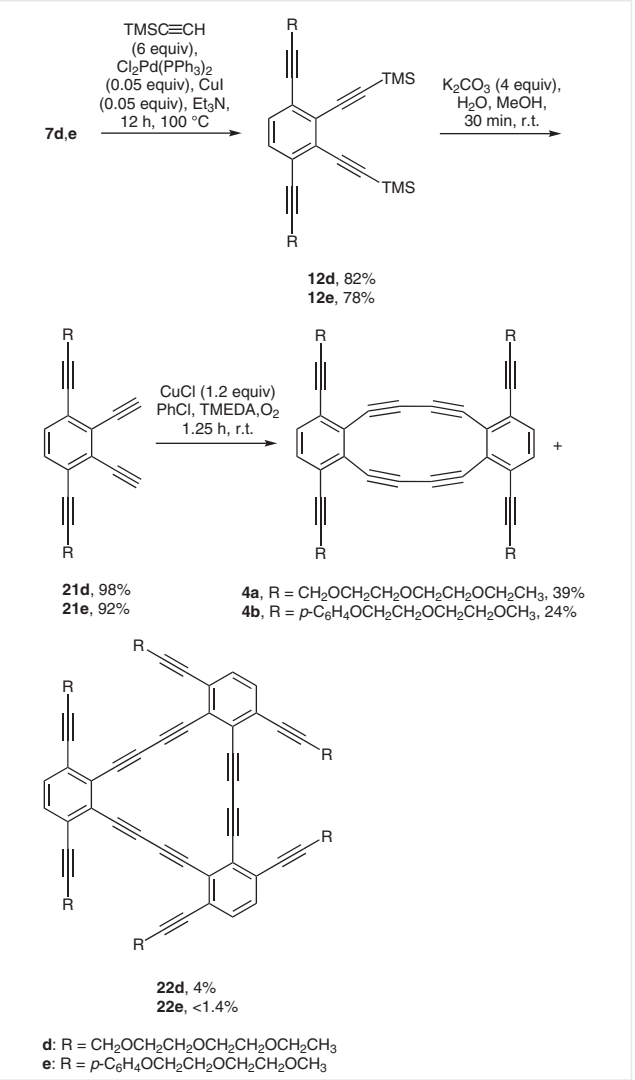
Nevertheless, with sufficient quantities of materials in hand, the next step was to convert the bromine substituent in **11d**,**e** (and **13e**) into iodine, necessary because the bromides appear to be unsuitable for the eventual cyclization to **2d**,**e**.[14] The hope that alcohol **15d** would prove to be an exception (vide supra) evaporated, when its treatment with aqueous NaOH and Pd-Cu catalysts under phase-transfer conditions[12] led to only decomposition. Therefore, as shown in Scheme 4, **11d**,**e** were subjected to the same sequence used for the conversion of **7d**,**e** into **17d**,**e** (Scheme 3), providing the iodoarenes **18d**,**e**, which were then deprotected to **20d**,**e**. Similarly, **13e** from Scheme 2 could be engaged to augment the supply of **20e** via bromine–iodine exchange to **19e** (78%), the TIPS analogue of **18e** (see experimental section), and its protodesilylation employing TBAF (97%). Finally, **20d**,**e** transformed to air stable **2d**,**e** by Stephens–Castro coupling[2a,15] in moderate yields (Scheme 4). Their D_{3h} symmetry is evident in their relatively simple NMR spectra. Like their relatives **2a–c**, they are yellow materials (**2d**: oil; **3e**: solid), exhibiting intense yellow-green fluorescence (for the fluorescence data, see experimental section).[16] As expected, these macrocycles (as well as all of the precursors in their synthesis) are very soluble in polar solvents and only sparingly so in nonpolar media. One notes that this and prior steps do not seem the benefit from the presence of the potentially chelating oligoether appendages when compared to those featured in the routes to **2a–c**.[2a]



Scheme 4 Preparation of targets **2d**,**e** through bromine–iodine exchange of **11d**,**e** to give **18d**,**e**, subsequent deprotection, and cyclization

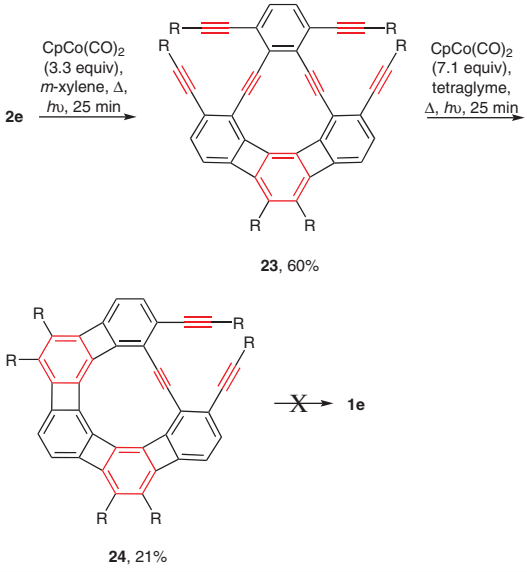
The availability of the tetraalkynylarenes **12d**,**e** and **14e** (albeit as side products of the synthesis of **11d**,**e** and **13e**, respectively; Scheme 2) suggested a ready test of the viability of the retrosynthetic analysis **3** ⇒ **4** (Figure 1), as their deprotected versions should lead to the required benzocyclyne **4** by oxidative dimerization.[14b] Consequently,

improved preparations of these materials were developed (Scheme 5), applying excess silylalkyne for the couplings with dibromides **7d**,**e** and furnishing good quantities of **12d** (82%), **12e** (78%), and **14e** (57%; see experimental section). Desilylation of all proceeded nearly quantitatively on treatment with basic MeOH (Scheme 5) or TBAF (for **14e**, see experimental section) to supply **21d**,**e**. The latter were then transformed into tetraynes **4a**,**b** under Hay conditions,[16k,l,17] generating minor amounts of the only partly characterized cyclic trimers **22d**,**e**.[2c] Compounds **4a**,**b** exist as sensitive, shiny yellow, fluorescent crystalline materials, very soluble in polar solvents and decomposing on melting.



Scheme 5 Synthesis of benzocyclynes **4a**,**b** and **22d**,**e** starting from dibromides **7d**,**e**

Having accessed the benzocyclynes in Figure 1, our attention turned to their CpCo-catalyzed (co)cyclizations. We chose **2e** as a first substrate, in which the phenylether substituents were expected to impart crystallinity. Disappointingly, the outcome of its exposure to excess $CpCo(CO)_2$ mimicked those observed previously with **2b** and **c**.[2a] Thus (Scheme 6), the first cycloisomerization took place quite well in boiling *m*-xylene (bp 139 °C) to provide the angular [3]phenylene frame of **23** in 60% yield. The second step to **24** needed the much higher temperature of boiling tetraglyme (bp 275 °C) to proceed, but attempted further conversion into **1e** reached an impasse from which the only escape was gradual decomposition on prolonged heating. The spectral data of **23** and **24** compare well with those of their propyl and cyclohexylmethyl analogues,[2a] in turn resting on the presence of highly diagnostic NMR and UV/Vis absorptions for the phenylene substructures.[4,18] These findings cement the original structural rationale for the failure to effect the conversion of **2** into **1**: The introduction of phenylene units causes the remaining triple bonds to be increasingly distant, posing an insurmountable barrier for the final cyclization.



Scheme 6 Attempted CpCo-catalyzed cycloisomerization of **2e** to **1e** via **23** and **24**

In view of this fiasco, further efforts along this strategy involving **2d** were abandoned, and our attention turned to the potential of the **4** + **5** → **3** approach (Figure 1), focusing first on the reaction of **4a** with **5a** (10 equivalents) in the presence of $CpCo(CO)_2$ (5 equivalents) in boiling *m*-xylene. Lamentably, this treatment led to extensive decomposition, without the generation of any identifiable material. To test the basic reactivity of **4a** in cocyclizations, the reaction was repeated with bis(trimethylsilyl)acetylene (BTMSA) in *m*-xylene (1:1). A complex mixture of CpCo complexes ensued, parceled into various fractions by repeated column chromatography and containing in part the known products derived from the reaction of BTMSA with $CpCo(CO)_2$ (^{1}H NMR), most prominently CpCo[1,2,3,4-tetrakis(trimethyl-

silyl)cyclobutadiene] (18% based on $CpCo(CO)_2$).[19] In addition, one fraction indicated the formation of a mixture of (mainly two) cyclobutadiene complexes derived from **4a** and BTMSA, as evidenced by sets of four doublets ($J \approx 8$ Hz) for the desymmetrized benzocyclyne frame and the corresponding CpCo and TMS singlets. Most telling was the absence of any relatively shielded ^{1}H NMR absorptions that would be have been expected for the angular [3]phenylene substructure. Consequently, this line of enquiry was terminated.

In conclusion, we have made available new alkyne synthetic building blocks containing oligoether substituents of potential use to researchers engaged in the exploration of supramolecular assemblies. In our efforts, these were elaborated to the benzocyclynes **2d**, **2e**, **4a**, and **4b**, with the aim to test their suitability as precursors to the antikekulenes **1d**, **1e**, **3a**, and **3b**. The substituents delivered on their promise to impart excellent solubility on these compounds, but did not do so with respect to improving the efficiency of the various Pd-, Cu-, and Co-mediated transformations. In particular, the specific aim to exploit them for the assembly of the antikekulene nucleus failed.

All reactions were carried out in degassed solvents under N_2 in flame-dried glassware. Unless otherwise noted, starting materials were obtained commercially and the solvents purified and dried applying common methods.[20] Et_3N, TMEDA, and pyridine were freshly distilled from KOH. Et_2O, DME, THF, and *m*-xylene were distilled from sodium benzophenone ketyl just prior to use. Chlorobenzene was dried by boiling over CaH_2. Silica gel (60–200 mesh) for column chromatography was purchased from ICN-Biomedicals. TLC was performed on Merck silica gel 60 F_{254} (aluminum foil). Mps were determined in open Pyrex capillaries on a Thomas Hoover melting point apparatus and are uncorrected. GC was carried out on a Hewlett Packard HP 5890 Series II instrument. UV-Visible spectra were recorded with CH_3CN solutions on a Hewlett Packard HP 8453 UV-Vis ChemStation. Fluorescence spectra were measured with MeCN solutions on an ISA/SPEX Fluorolog 3.22 spectrometer equipped with a 450-W Xe lamp. The samples were excited at the described wavelength, slit widths were set to 2 nm bandpass (excitation) and 3 nm bandpass (emission). IR spectra were obtained on films (NaCl) or KBr pellets with a Perkin-Elmer PE 2000 FT-IR spectral photometer. ^{1}H NMR and ^{13}C{H} spectra were recorded on Bruker DRX-500, AMX-400, AM-400, and AMX-300 spectrometers. When so specified, the extent of substitution on carbon was determined by APT (attached proton test) spectra. Mass data were provided by the UC Berkeley Mass Laboratory or were measured as GC-MS spectra on a Hewlett Packard HP 5970A mass detector instrument at 70 eV combined with the GC apparatus described above.

3-[2-(2-Ethoxyethoxy)ethoxy]prop-1-yne (6a)[8]

To a suspension of pure NaH (2.40 g, 100 mmol) in anhyd DME (100 mL) was slowly added 2-(2-ethoxyethoxy)ethanol (13.42 g, 100 mmol) at r.t. After stirring for 30 min, the now clear solution was treated with 3-bromoprop-1-yne (11.9 g, 100 mmol) in PhMe (2 mL) over a period of 15 min (violent reaction) with vigorous stirring. The resulting blend was heated to reflux for 4 h, allowed to cool to r.t., and filtered. Addition of H_2O (300 mL) was followed by extraction with CH_2Cl_2 (3 × 100 mL), and the organic layers were combined, washed with H_2O (3 × 100 mL), and dried ($MgSO_4$). Evaporation of the solvents under reduced pressure and vacuum distillation of the residual liquid gave **6a** as a colorless liquid; yield: 12.9 g (75%); bp 47–48 °C/0.1 Torr. Employment of prop-2-yn-1-yl 4-methylbenzenesulfonate in DME instead of 3-bromoprop-1-yne generated **6a** in only 40% yield.

IR (film): 3251, 2975, 2868, 2114, 1444, 1349, 1289, 1246, 1107, 1033, 948, 920, 844, 671 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.19 (d, *J* = 2.4 Hz, 2 H), 3.68 (AA′BB′m, 4 H), 3.64 (AA′m, 2 H), 3.58 (BB′m, 2 H), 3.51 (q, *J* = 7.0 Hz, 2 H), 2.40 (t, *J* = 2.4 Hz, 1 H), 1.19 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.3 (CH), 74.3 (C_{quat}), 70.4 (CH_2), 70.1 (CH_2), 69.5 (CH_2), 68.8 (CH_2), 66.3 (CH_2), 58.0 (CH_2), 14.8 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 173 ([MH$^+$], 55), 127 (10), 117 (10), 103 (20), 83 (40), 73 (100), 59 (70).

HRMS (EI, 70 eV): *m*/*z* [MH$^+$] calcd for $C_9H_{17}O_3$: 173.1178; found: 173.1173.

1-Ethynyl-4-[2-(2-methoxyethoxy)ethoxy]benzene (6b)[9]

To a suspension of pure NaH (1.20 g, 50 mmol) in anhyd DME (100 mL) was added slowly a solution of 4-iodophenol (11.0 g, 50 mmol) in anhyd DME (50 mL) at r.t. to give a clear solution after stirring for 30 min. This mixture was treated with 1-bromo-2-(2-methoxyethoxy)ethane (6.80 mL, 9.25 g, 50 mmol) in one portion with vigorous stirring, followed by boiling for 3 h, cooling to r.t., filtration, solvent evaporation under reduced pressure, and vacuum distillation to render 1-iodo-4-[2-(2-methoxyethoxy)ethoxy]benzene as a light-sensitive, colorless, glass-like solid; yield: 12.8 g (79%); mp 35–45 °C; bp 133–135 °C/0.25 Torr. The product can also be purified by column chromatography (silica gel, EtOAc/hexane 1:1).

IR (film): 2924, 2877, 2824, 1587, 1486, 1454, 1401, 1355, 1331, 1283, 1246, 1200, 1176, 1111, 1058, 1030, 1000, 940, 924, 822, 695, 636, 585 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 9.0 Hz, 2 H), 6.69 (d, *J* = 9.0 Hz, 2 H), 4.09 (AA′m, 2 H), 3.84 (BB′m, 2 H), 3.70 (AA′m, 2 H), 3.57 (BB′m, 2 H), 3.38 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6 (C_{quat}), 138.1 (CH), 117.0 (CH), 82.9 (C_{quat}), 71.9 (CH_2), 70.7 (CH_2), 69.6 (CH_2), 67.5 (CH_2), 59.1 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 322 ([M$^+$], 100), 246 (10), 220 (20), 203 (55), 150 (5), 120 (15), 103 (40), 76 (15), 59 (85).

At r.t., a solution of (trimethylsilyl)acetylene (6.40 mL, 4.42 g, 45 mmol,) in Et_3N (20 mL) was injected into a Fisher–Porter vessel containing 1-iodo-4-[2-(2-methoxyethoxy)ethoxy]benzene (11.9 g, 37 mmol), $Cl_2Pd(PPh_3)_2$ (702 mg, 1.00 mmol), and CuI (190 mg, 1.00 mmol) in Et_3N (130 mL). The bottle was sealed and the mixture stirred for 24 h at r.t., followed by 2 h at 50 °C. During this time, the solution turned bright yellow rapidly, then yellow-brown, and finally dark brown with the formation of a precipitate. After filtration, the solvent was evaporated in vacuo and the resulting residue purified by column chromatography (silica gel, hexane/EtOAc 2:1) to furnish 1-[2-(2-methoxyethoxy)ethoxy]-4-[(trimethylsilyl)ethynyl]benzene as a colorless oil; yield: 10.44 g (96%).

IR (film): 3043, 2958, 2927, 2879, 2822, 2156, 1605, 1570, 1507, 1455, 1411, 1356, 1331, 1288, 1250, 1200, 1173, 1111, 1062, 925, 866, 842, 761, 699, 638, 542 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.8 Hz, 2 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 4.14 (AA′m, 2 H), 3.86 (BB′m, 2 H), 3.72 (AA′m, 2 H), 3.58 (BB′m, 2 H), 3.40 (s, 3 H), 0.23 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6 (C_{quat}), 133.0 (CH), 115.0 (C_{quat}), 114.1 (CH), 104.9 (C_{quat}), 92.0 (C_{quat}), 71.5 (CH_2), 70.3 (CH_2), 69.2 (CH_2), 67.0 (CH_2), 58.6 (CH_3), –0.27 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 292 ([M$^+$], 100), 233 (5), 175 (40), 103 (30), 89 (10), 73 (5), 59 (55).

To a solution of 1-[2-(2-methoxyethoxy)ethoxy]-4-[(trimethylsilyl)ethynyl]benzene (10.2 g, 35 mmol) in MeOH (200 mL) was added sat. aq K_2CO_3 (5 mL, 40 mmol) at r.t. The resulting cloudy solution was stirred until clear (approx. 1 h, TLC monitoring), diluted with CH_2Cl_2 (200 mL), washed with H_2O (3 × 100 mL), dried ($MgSO_4$), and the volatiles were removed under reduced pressure. The crude material was purified by column chromatography (silica gel, hexane/EtOAc 2:1) to supply **6b** as a colorless oil; yield: 7.15 g (93%).

IR (film): 3285, 3072, 3042, 2926, 2879, 2824, 2106, 1606, 1571, 1505, 1455, 1355, 1289, 1249, 1200, 1172, 1110, 1061, 1030, 925, 835, 702, 659, 642 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.8 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 4.14 (AA′m, 2 H), 3.86 (BB′m, 2 H), 3.72 (AA′m, 2 H), 3.57 (BB′m, 2 H), 3.39 (s, 3 H), 2.99 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8 (C_{quat}), 133.1 (CH), 114.2 (CH), 113.9 (C_{quat}), 83.3 (C_{quat}), 75.8 (CH), 71.5 (CH_2), 70.3 (CH_2), 69.2 (CH_2), 67.0 (CH_2), 58.6 (CH_3).

MS (FAB, 70 eV): *m*/*z* (%) = 221 ([MH$^+$]).

HRMS (FAB, 70 eV): *m*/*z* [M$^+$] calcd for $C_{13}H_{16}O_3$: 221.1099; found: 221.1103.

2,3-Dibromo-1,4-bis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}benzene (7d)

Alkyne 6a (4.30 g, 25 mmol) in Et_3N (50 mL) was injected into a Fisher–Porter vessel containing a mixture of 1,2,3,4-tetrabromobenzene[10] (3.94 g, 10 mmol), $Cl_2Pd(PPh_3)_2$ (176 mg, 0.25 mmol), and CuI (48 mg, 0.25 mmol) in Et_3N (100 mL) at r.t. The mixture was stirred for 12 h at 70 °C, during which it turned rapidly bright yellow, then yellow-brown, and finally dark brown with the formation of a precipitate. The suspension was cooled to r.t., filtered, and the volatiles removed in vacuo. The resulting residue was purified by column chromatography (silica gel, Et_2O) to separate first the monoalkynylated constituent 1,2,3-tribromo-4-{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}benzene (8d) as a light yellow oil; yield: 600 mg (12%).

IR (film): 3073, 2973, 2867, 2224, 1563, 1485, 1456, 1430, 1374, 1340, 1287, 1271, 1242, 1103, 1054, 1031, 976, 946, 817, 787, 722 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.3 Hz, 1 H), 7.24 (d, *J* = 8.3 Hz, 1 H), 4.45 (s, 2 H), 3.79 (AA′M, 2 H), 3.70 (BB′m, 2 H), 3.64 (AA′m, 2 H), 3.58 (BB′m, 2 H), 3.51 (q, *J* = 7.0 Hz, 2 H), 1.19 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.1, 131.7, 129.1, 128.2, 125.9, 125.8, 91.3, 84.5, 70.6, 70.3, 69.7, 69.2, 66.5, 58.9, 15.1.

MS (EI, 70 eV): *m*/*z* (%) = 486 ([M$^+$], 2), 484 ([M$^+$], 2), 456 (2), 454 (2), 440 (2), 438 (2), 427 (10), 425 (10), 413 (2), 411 (2), 353 (57), 351 (57), 274 (18), 272 (18), 193 (20), 191 (20), 116 (17), 73 (64), 72 (100), 59 (40).

HRMS (EI, 70 eV): *m*/*z* [M$^+$] calcd for $C_{15}H_{17}{}^{79}Br_3O_3$: 481.8728; found: 481.8728.

UV/VIS (MeCN): λ_{max} (log ε) = 224 (4.55), 257 (4.28), 269 nm (4.24).

A second fraction furnished dialkynylated product **7d** as a light yellow oil; yield: 3.50 g (61%).

IR (film): 2974, 2868, 2220, 1577, 1485, 1449, 1375, 1351, 1289, 1245, 1107, 1032, 971, 945, 841, 733, 666 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (s, 2 H), 4.48 (s, 4 H), 3.79 (AA′ m, 4 H), 3.71 (BB′m, 4 H), 3.66 (AA′m, 4 H), 3.59 (BB′m, 4 H), 3.51 (q, *J* = 7.0 Hz, 4 H), 1.20 (t, *J* = 7.0 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.2, 128.4, 126.5, 92.0, 84.8, 70.5, 70.3, 69.6, 69.1, 66.4, 58.9, 15.0.

MS (EI, 70 eV): *m*/*z* (%) = 576 ([M$^+$], 2), 503 (10), 442 (19), 327 (15), 311 (26), 217 (20), 150 (28), 117 (50), 103 (75), 89 (58), 73 (100), 59 (40).

HRMS (EI, 70 eV): *m*/*z* [M$^+$] calcd for $C_{24}H_{32}{}^{79}Br_2O_6$: 574.0566; found: 574.0567.

UV/VIS (MeCN): λ_{max} (log ε) = 222 (4.34), 229 (4.35), 277 (4.39), 289 nm (4.51).

The last fraction gave rise to trialkynylated ingredient 2-bromo-1,3,4-tris{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}benzene (**9d**) as a yellow oil; yield: 1.20 g (18%).

IR (film): 2974, 2868, 2228, 1578, 1486, 1458, 1385, 1349, 1292, 1267, 1246, 1209, 1099, 1056, 1030, 977, 947, 843, 763, 669 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (s, 2 H), 4.50 (s, 2 H), 4.47 (s, 2 H), 4.45 (s, 2 H), 3.85–3.75 (m, 6 H), 3.72–3.69 (m, 6 H), 3.67–3.63 (m, 6 H), 3.61–3.56 (m, 6 H), 3.52 (q, *J* = 7.0 Hz, 2 H), 3.51 (q, *J* = 7.0 Hz, 4 H), 1.19 (t, *J* = 7.0 Hz, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 131.8, 130.2, 128.3, 127.6, 126.4, 125.3, 94.3, 91.6, 91.4, 84.3, 84.0, 83.5, 70.5 (3 C), 70.2 (3 C), 69.6 (3 C), 69.1, 69.0, 68.9, 66.4 (3 C), 58.8 (br, 3 C), 14.9 (3 C).

MS (EI, 70 eV): *m*/*z* (%) = 534 ([M$^+$], 4), 532 ([M$^+$], 4), 461 (1), 459 (1), 117 (20), 73 (55), 59 (100).

MS (FAB, 70 eV): *m*/*z* (%) = 669 ([MH$^+$]), 667 ([MH$^+$]).

HRMS (FAB, 70 eV): *m*/*z* [MH$^+$] calcd for $C_{33}H_{48}{}^{81}BrO_9$: 669.2461); found: 669.2457.

UV/VIS (MeCN): λ_{max} (log ε) = 247 (4.60), 254 (4.67), 277 (4.33), 283 (4.36), 294 nm (4.49).

2,3-Dibromo-1,4-bis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}benzene (7d) by Alkynylation of 8d

Monoalkynylated **8d** (4.85 g, 10 mmol) was exposed to **6a** (3.80 g, 22 mmol) as in the preceding preparation of **7d**, except that the reaction temperature was kept at 100 °C, to engender, in order of elution on chromatography, **7d**; yield: 4.37 g (65%); **9d**; yield: 1.27 g (19%); and the tetraalkynylated product 1,2,3,4-tetrakis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}benzene (**10d**) as a yellow oil; yield: 610 mg (8%).

IR (film): 2974, 2868, 2227, 1486, 1462, 1408, 1349, 1297, 1245, 1106, 1049, 1029, 947, 845 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (s, 2 H), 4.48 (s, 4 H), 4.44 (s, 4 H), 3.81–3.75 (m, 8 H), 3.69–3.62 (m, 16 H), 3.61–3.57 (m, 8 H), 3.51 (q, *J* = 7.1 Hz, 4 H), 3.50 (q, *J* = 7.1 Hz, 4 H), 1.191 (t, *J* = 7.1 Hz, 6 H), 1.187 (t, *J* = 7.1 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 131.1, 127.7, 125.3, 93.5, 90.9, 84.1, 83.2, 70.54, 70.53, 70.3 (2 C), 69.6 (2 C), 69.0, 68.8, 66.4 (2 C), 58.92, 58.89, 15.0 (2 C).

MS (EI, 70 eV): *m*/*z* (%) = 758 ([M$^+$], 0.2), 624 (3), 552 (25), 117 (45), 103 (20), 73 (75), 59 (100).

UV/VIS (MeCN): λ_{max} (log ε) = 254 (sh, 4.60), 256 (sh, 4.65), 263 (4.77), 277 (4.47), 285 (4.28), 296 nm (4.47).

2,3-Dibromo-1,4-bis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)benzene (7e)

Following the procedure employed for the preparation of **7d**, treatment of 1,2,3,4-tetrabromobenzene[10] (3.94 g, 10 mmol) with alkyne **6b** (4.88 g, 22 mmol) and column chromatography (silica gel, EtOAc) produced a first fraction containing 1,2,3-tribromo-4-({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)benzene (**8e**) as colorless crystals; yield: 1.35 g (25%); mp 84 °C (EtOH).

IR (KBr): 2985, 2951, 2925, 2889, 2856, 2816, 2224, 1605, 1561, 1509, 1456, 1429, 1384, 1363, 1340, 1283, 1250, 1167, 1140, 1114, 1085, 1058, 1021, 936, 916, 848, 823, 724, 562, 532 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.4 Hz, 1 H), 7.49 (d, *J* = 8.8 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 4.17 (AA′m, 2 H), 3.87 (BB′m, 2 H), 3.72 (AA′m, 2 H), 3.58 (BB′m, 2 H), 3.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 133.2, 131.8, 131.6, 128.9, 128.2, 126.9, 125.1, 114.7, 114.5, 95.5, 86.9, 71.9, 70.7, 69.6, 67.4, 59.0.

MS (EI, 70 eV): *m*/*z* (%) = 534 ([M^+], 65), 532 ([M^+], 65), 432 (16), 430 (16), 243 (6), 241 (6), 174 (8), 103 (30), 59 (100).

HRMS (EI, 70 eV): *m*/*z* [M^+] calcd for $C_{19}H_{17}{}^{81}Br_3O_3$: 535.8667; found: 535.8667.

UV/VIS (MeCN): λ_{max} (log ε) = 218 (4.32), 244 (4.00), 254 (3.93), 272 (3.89), 309 (4.37), 324 nm (4.38).

The second fraction consisted of **7e** as colorless flakes; yield: 3.86 g (57%); mp 96–97 °C (EtOH).

IR (KBr): 3070, 3041, 2988, 2875, 2824, 2226, 2212, 1602, 1571, 1542, 1516, 1473, 1458, 1383, 1351, 1332, 1303, 1286, 1251, 1197, 1167, 1145, 1123, 1101, 1062, 1030, 955, 925, 911, 885, 855, 844, 828, 811, 789, 708, 644, 627, 537 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.9 Hz, 4 H), 7.42 (s, 2 H), 6.91 (d, *J* = 8.9 Hz, 4 H), 4.17 (AA′m, 4 H), 3.87 (BB′m, 4 H), 3.73 (AA′m, 4 H), 3.58 (BB′m, 4 H), 3.40 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 133.1, 130.6, 128.1, 126.7, 114.6, 114.5, 96.0, 87.4, 71.7, 70.6, 69.4, 67.3, 58.9.

MS (EI, 70 eV): *m*/*z* (%) = 672 ([M^+], 100), 569 (5), 103 (15), 59 (60).

HRMS (EI, 70 eV): *m*/*z* [M^+] calcd for $C_{32}H_{32}{}^{79}Br^{81}BrO_6$: 672.0545; found: 672.0543.

UV/VIS (MeCN): λ_{max} (log ε) = 215 (sh, 4.61), 239 (4.50), 248 (4.49), 345 (4.82), 361 nm (sh, 4.76).

A third fraction was comprised of 3-bromo-1,2,4-tris({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)benzene (**9e**) as light yellow waxy crystals; yield: 820 mg (10%); mp 40–50 °C (EtOH).

IR (KBr): 2928, 2877, 2824, 2215, 1604, 1571, 1514, 1456, 1357, 1287, 1250, 1200, 1166, 1111, 1059, 924, 829, 647, 612, 535 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 9.2 Hz, 2 H), 7.51 (d, *J* = 9.2 Hz, 2 H), 7.47 (d, *J* = 9.2 Hz, 2 H), 7.42 (ABq, *J* = 8.2 Hz, 2 H), 6.905 (d, *J* = 8.8 Hz, 2 H), 6.897 (d, *J* = 8.8 Hz, 2 H), 6.885 (d, *J* = 9.2 Hz, 2 H), 4.16 (m, 6 H), 3.87 (m, 6 H), 3.73 (m, 6 H), 3.58 (m, 6 H), 3.395 (s, 3 H), 3.393 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 159.22, 159.19, 159.15, 133.13, 133.12, 133.08, 130.9, 129.7, 128.3, 127.8, 126.4, 125.6, 115.1, 115.0, 114.8, 114.63, 114.61 (2 C), 98.4, 95.8, 95.6, 87.2, 86.9, 86.5, 71.8 (3 C), 70.6 (3 C), 69.5 (3 C), 67.4 (3 C), 59.0 (3 C).

MS (EI, 70 eV): *m*/*z* (%) = 812 ([M^+], 10), 810 ([M^+], 10), 594 (30), 592 (30), 277 (50), 107 (30), 95 (75), 59 (100).

UV/VIS (MeCN): λ_{max} (log ε) = 228 (4.51), 234 (sh, 4.50), 286 (sh, 4.48), 322 (4.79), 343 (sh, 4.66), 361 nm (sh, 4.61).

Compound **7e** could also be made by alkynylation of **8e** following the protocol used for the conversion of **8d** to give **7d**, **9d**, and **10d** (vide supra) to afford **7e** (59%) and **9e** (21%), but no **10e**.

2-Bromo-1,4-bis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}-3-[(trimethylsilyl)ethynyl]benzene (11d)

(Trimethylsilyl)acetylene (0.75 mL, 520 mg, 5.30 mmol) in Et_3N (10 mL) was injected into a Fisher–Porter vessel containing **7d** (2.88 g, 5.00 mmol), $Cl_2Pd(PPh_3)_2$ (176 mg, 0.25 mmol), and CuI (48 mg, 0.25 mmol) in Et_3N (100 mL) at r.t. The vessel was sealed and the mixture heated at 100 °C for 12 h. Column chromatography (silica gel, Et_2O), supplied a first fraction containing 1,4-bis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}-2,3-bis[(trimethylsilyl)ethynyl]benzene (**12d**) as a yellow oil; yield: 300 mg (10%).

IR (film): 2960, 2868, 2157, 1486, 1460, 1394, 1376, 1349, 1287, 1250, 1178, 1101, 1034, 885, 842, 761, 713, 699, 626 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 2 H), 4.46 (s, 4 H), 3.78 (AA′m, 4 H), 3.70 (BB′m, 4 H), 3.65 (AA′m, 4 H), 3.59 (BB′m, 4 H), 3.51 (q, *J* = 7.0 Hz, 4 H), 1.19 (t, ^3J = 7.0 Hz, 6 H), 0.25 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.0, 128.4, 125.5, 103.6, 101.2, 90.8, 84.2, 70.6, 70.4, 69.7, 69.1, 66.5, 59.0, 15.1, –0.14.

MS (EI, 70 eV): *m*/*z* (%) = 610 ([M^+], 5), 537 (10), 493 (20), 476 (40), 147 (8), 117 (40), 103 (8), 73 (100), 59 (15).

HRMS (EI, 70 eV): *m*/*z* [M^+] calcd for $C_{34}H_{50}O_6Si_2$: 610.3146; found: 610.3160.

UV/VIS (MeCN): λ_{max} (log ε) = 257 (sh, 4.48), 262 (sh, 4.73), 269 (4.90), 282 (4.64), 287 (sh, 4.55), 298 nm (4.46).

The second fraction delivered **11d** as a yellow oil; yield: 560 mg (19%).

IR (film): 2973, 2867, 2223, 2158, 1577, 1486, 1456, 1377, 1349, 1290, 1250, 1192, 1109, 1035, 977, 945, 883, 847, 760, 701, 684, 663, 624 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (ABq, 2 H), 4.45 (s, 4 H), 3.77 (m, 4 H), 3.71 (m, 4 H), 3.65 (m, 4 H), 3.59 (m, 4 H), 3.53 (q, *J* = 7.0 Hz, 2 H), 3.51 (q, *J* = 7.0 Hz, 2 H), 1.195 (t, *J* = 7.0 Hz, 3 H), 1.191 (t, *J* = 7.0 Hz, 3 H), 0.26 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 31.9, 130.3, 128.6, 128.2, 126.7, 125.4, 104.7, 101.4, 91.6, 91.5, 84.6, 84.1, 70.65, 70.62, 70.4 (2 C), 69.7 (2 C), 69.2 (2 C), 66.6 (2 C), 59.01, 58.98, 15.1, –0.26.

MS (EI, 70 eV): *m*/*z* (%) = 594 ([M^+], 2), 592 ([M^+], 2), 535 (2), 533 (2), 521 (5), 519 (5), 491 (2), 489 (2), 477 (15), 475 (15), 460 (20), 458 (20), 117 (60), 73 (100), 59 (25).

HRMS (EI, 70 eV): *m*/*z* [M^+] calcd for $C_{29}H_{41}{}^{79}BrO_6Si$: 592.1856; found: 592.1851.

UV/VIS (MeCN): λ_{max} (log ε) = 241 (sh, 4.42), 246 (sh, 4.56), 250 (4.59), 258 (4.77), 279 (4.32), 286 (4.35), 296 nm (4.44).

A third fraction returned starting material **7d**; yield: 1.50 g (66%).

3-Bromo-1,4-bis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)-2-[(trimethylsilyl)ethynyl]benzene (11e)

The procedure for the preparation of **11d** was replicated, but starting with **7e** (3.36 g, 5 mmol). Column chromatography (silica gel, Et_2O) furnished a first fraction containing 1,4-bis({4-[2-(2-methoxy-

ethoxy)ethoxy]phenyl}ethynyl)-2,3-bis[(trimethylsilyl)ethynyl]benzene (**12e**) as light yellow needles; yield: 100 mg (3%); mp 100–101 °C dec (MeOH).

IR (KBr): 2959, 2874, 2826, 2210, 1602, 1510, 1458, 1392, 1355, 1283, 1250, 1198, 1166, 1144, 1123, 1110, 1059, 1030, 1013, 954, 940, 922, 846, 811, 762, 677, 618, 541 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.8 Hz, 4 H), 7.37 (s, 2 H), 6.89 (d, *J* = 8.8 Hz, 4 H), 4.16 (AA′m, 4 H), 3.87 (BB′m, 4 H), 3.72 (AA′m, 4 H), 3.58 (BB′m, 4 H), 3.39 (s, 6 H), 0.29 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 133.2, 130.6, 128.1, 125.9, 115.3, 114.6, 103.9, 101.6, 95.2, 86.8, 71.9, 70.8, 69.6, 67.5, 59.1, 0.06.

MS (EI, 70 eV): *m*/*z* (%) = 706 ([M⁺], 100), 603 (10), 59 (15).

HRMS (EI, 70 eV): *m*/*z* [M⁺] calcd for $C_{42}H_{50}O_6Si_2$: 706.3146; found: 706.3160.

UV/VIS (MeCN): λ_{max} (log ε) = 263 (sh, 4.56), 273 (4.62), 287 (4.66), 348 (4.70), 361 nm (sh, 4.66).

The second fraction revealed **11e** as colorless needles; yield: 710 mg (21%); mp 66–67 °C (MeOH).

IR (KBr): 3073, 2929, 2874, 2825, 2217, 1603, 1522, 1509, 1457, 1380, 1354, 1289, 1251, 1166, 1145, 1125, 1111, 1060, 1030, 974, 955, 923, 845, 761, 671, 619, 536 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.8 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 7.39 (br s, 2 H), 6.91 (AA′m, 2 H), 6.89 (BB′m, 2 H), 4.17 (AA′m, 4 H), 3.87 (BB′m, 4 H), 3.73 (AA′m, 4 H), 3.58 (BB′m, 4 H), 3.40 (br s, 6 H), 0.30 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 159.23, 159.18, 133.2 (2 C), 131.5, 129.2, 128.4, 127.7, 127.0, 125.6, 115.0, 114.8, 114.64, 114.59, 104.3, 101.8, 95.8, 95.6, 87.1, 86.7, 71.8 (2 C), 70.7 (2 C), 69.6 (2 C), 67.4 (2 C), 59.0 (2 C), –0.17.

MS (EI, 70 eV): *m*/*z* (%) = 690 ([M⁺], 50), 688 ([M⁺], 50), 587 (20), 585 (20), 103 (30), 59 (100).

HRMS (EI, 70 eV): *m*/*z* [M⁺] calcd for $C_{37}H_{41}{}^{81}BrO_6Si$: 690.1850; found: 690.1855.

UV/VIS (MeCN): λ_{max} (log ε) = 251 (4.58), 275 (4.60), 343 (4.75), 353 nm (sh, 4.73).

The third fraction led to recovered starting material **7e**; yield: 2.46 g (73%).

3-Bromo-1,4-bis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)-2-[(triisopropylsilyl)ethynyl]benzene (13e)

(Triisopropylsilyl)acetylene (1.23 mL, 1.00 g, 5.48 mmol) was reacted with **7e** (3.36 g, 5.00 mmol) following the experimental procedure for the preparation of **7d**. Column chromatography (silica gel, EtOAc) led first to 1,4-bis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)-2,3-bis[(triisopropylsilyl)ethynyl]benzene (**14e**) as light yellow needles; yield: 48 mg (1%); mp 65–66 °C (EtOH).

IR (KBr): 2942, 2889, 2865, 2214, 2134, 1604, 1510, 1457, 1392, 1353, 1286, 1248, 1200, 1169, 1142, 1127, 1110, 1061, 999, 951, 936, 923, 883, 836, 754, 679, 612, 592, 541 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.8 Hz, 4 H), 7.40 (s, 2 H), 6.87 (d, *J* = 8.8 Hz, 4 H), 4.17 (AA′m, 4 H), 3.88 (BB′m, 4 H), 3.73 (AA′m, 4 H), 3.59 (BB′m, 4 H), 3.40 (s, 6 H), 1.10 (m, 42 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 133.1, 131.5, 127.6, 127.0, 115.4, 114.4, 103.3, 100.3, 94.8, 86.9, 71.9, 70.7, 69.6, 67.4, 59.0, 18.7, 11.4.

MS (FAB, 70 eV): *m*/*z* (%) = 875 ([MH⁺]).

UV/VIS (MeCN): λ_{max} (log ε) = 266 (sh, 4.60), 275 (4.68), 290 (4.71), 345 nm (4.59).

Next to be eluted was **13e**, forming colorless crystals; yield: 1.07 g (28%); mp 108 °C dec (EtOH).

IR (KBr): 3061, 2941, 2865, 2220, 1602, 1510, 1455, 1378, 1357, 1287, 1246, 1233, 1203, 1170, 1140, 1111, 1060, 1018, 970, 950, 922, 882, 842, 830, 811, 680, 648, 604, 538, 509 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.8 Hz, 2 H), 7.44 (d, *J* = 8.8 Hz, 2 H), 7.40 (ABq, 2 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 4.17 (AA′m, 4 H), 3.88 (BB′m, 4 H), 3.73 (AA′m, 4 H), 3.59 (BB′m, 4 H), 3.40 (s, 6 H), 1.15 (m, 21 H).

^{13}C NMR (100 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 159.3, 159.1, 133.20, 133.14, 131.2, 130.3, 129.0, 127.9, 127.0, 125.7, 115.1, 114.9, 114.7, 114.5, 103.5, 101.3, 95.6, 95.5, 87.2, 86.7, 71.9 (2 C), 70.7 (2 C), 69.59, 69.57, 67.4 (2 C), 59.0 (2 C), 18.7, 11.3.

MS (EI, 70 eV): *m*/*z* (%) = 774 ([M⁺], 60), 772 ([M⁺], 60), 262 (100), 183 (46), 59 (50).

UV/VIS (MeCN): λ_{max} (log ε) = 252 (4.53), 277 (4.54), 343 (4.68), 359 nm (sh, 4.61).

A last fraction contained recovered **7e**; yield: 2.02 g (60%).

4-(2-Bromo-3,6-bis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}phenyl)-2-methylbut-3-yn-2-ol (15d)

2-Methylbut-3-yn-2-ol (750 µL, 650 mg, 7.70 mmol) was reacted with **7d** (1.73 g, 3.00 mmol), following the experimental procedure for the preparation of **7d**. Column chromatography (silica gel, Et_2O) separated first starting material **7d**; yield: 674 mg (39%); followed by **15d** as a yellow oil; yield: 633 mg (36%).

IR (film): 3427, 2977, 2924, 2869, 2228, 1579, 1485, 1456, 1372, 1349, 1291, 1268, 1243, 1154, 1105, 1029, 963, 917, 840, 789, 748, 708, 666 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.30 (ABq, 2 H), 4.48 (br s, 4 H), 3.81 (AA′m, 4 H), 3.72 (BB′m, 4 H), 3.67 (AA′m, 4 H), 3.60 (BB′m, 4 H), 3.531 (q, *J* = 7.0 Hz, 2 H), 3.524 (q, *J* = 7.0 Hz, 2 H), 1.64 (s, 6 H), 1.208 (t, *J* = 7.0 Hz, 3 H), 1.202 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 131.6 (CH), 129.7 (CH), 128.1 (C_{quat}), 128.0 (C_{quat}), 126.3 (C_{quat}), 125.2 (C_{quat}), 103.5 (C_{quat}), 91.5 (C_{quat}), 91.3 (C_{quat}), 84.4 (C_{quat}), 84.2 (C_{quat}), 79.4 (C_{quat}), 70.5 (CH_2, 2 C), 70.2 (CH_2, 2 C), 69.57 (CH_2), 69.49 (CH_2), 69.12 (CH_2), 69.04 (CH_2), 66.4 (CH_2, 2 C), 65.1 (C_{quat}), 58.99 (CH_2), 58.85 (CH_2), 31.1 (CH_3), 14.97 (CH_3), 14.94 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 580 ([M⁺], 0.2), 578 ([M⁺], 0.2), 562 (30), 560 (30), 489 (10), 487 (10), 428 (20), 426 (20), 189 (44), 117 (70), 73 (100), 59 (60).

UV/VIS (MeCN): λ_{max} (log ε) = 248 (4.61), 255 (4.69), 277 (4.34), 284 (4.37), 294 nm (4.49).

Eluting the column with EtOAc gave 4,4′-(3,6-bis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}-1,2-phenylene)bis(2-methylbut-3-yn-2-ol) (**16d**) as a yellow oil; yield: 160 mg (9%).

IR (film): 3416, 2978, 2930, 2868, 2227, 1461, 1407, 1350, 1294, 1252, 1224, 1170, 1104, 1036, 963, 919, 841, 769, 741, 673 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.27 (s, 2 H), 4.47 (s, 4 H), 3.81 (AA′m, 4 H), 3.72 (BB′m, 4 H), 3.66 (AA′m, 4 H), 3.60 (BB′m, 4 H), 3.52 (q, *J* = 7.0 Hz, 4 H), 2.51 (v br s, 2 H), 1.63 (s, 12 H), 1.20 (t, *J* = 7.0 Hz, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 130.4 (CH), 128.1 (C_{quat}), 124.9 (C_{quat}), 102.8 (C_{quat}), 90.6 (C_{quat}), 84.4 (C_{quat}), 79.1 (C_{quat}), 70.6 (CH_2), 70.3 (CH_2), 69.6 (CH_2), 69.1 (CH_2), 66.5 (CH_2), 65.3 (C_{quat}), 59.1 (CH_2), 31.3 (CH_3), 15.0 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 564 ([M$^+$ – H_2O], 40), 491 (10), 297 (22), 283 (18), 281 (17), 269 (18), 253 (28), 239 (48), 226 (34), 215 (24), 213 (18), 202 (18), 189 (14), 117 (40), 103 (10), 73 (70), 59 (100).

UV/VIS (MeCN): λ_{max} (log ε) = 253 (sh, 4.58), 256 (sh, 4.63), 263 (4.79), 277 (4.47), 285 (4.27), 296 nm (4.45).

2-Bromo-1,4-bis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}-3-iodobenzene (17d)

To **7d** (1.44 g, 2.50 mmol) in anhyd Et_2O (100 mL) was added 1.6 M BuLi in hexane (1.9 mL, 3.0 mmol) at –110 °C. After stirring for 1 h, I_2 (950 mg, 3.74 mmol) in anhyd Et_2O (50 mL) was dripped in via cannula. The mixture was stirred for an additional 30 min at –110 °C and then allowed to warm to r.t. The resulting solution was washed first with sat. aq $Na_2S_2O_3$, then H_2O, and dried ($MgSO_4$). The volatiles were removed in vacuo and the residue subjected to column chromatography (silica gel, Et_2O) to render **17d** as a light yellow oil; yield: 1.00 g (64%).

IR (film): 2973, 2868, 2218, 1573, 1485, 1442, 1375, 1347, 1288, 1263, 1246, 1104, 1031, 967, 947, 840, 801, 723, 658 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.0 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 1 H), 4.49 (s, 2 H), 4.48 (s, 2 H), 3.84–3.77 (m, 4 H), 3.75–3.69 (m, 4 H), 3.69–3.63 (m, 4 H), 3.63–3.57 (m, 4 H), 3.52 (q, *J* = 7.0 Hz, 4 H), 1.20 (t, *J* = 7.0 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 133.2, 132.2, 131.6, 130.4, 125.3, 108.6, 91.6, 91.1, 88.8, 85.4, 70.6 (2 C), 70.3 (2 C), 69.7 (2 C), 69.3, 69.2, 66.5 (2 C), 58.9 (2 C), 15.1 (2 C).

MS (EI, 70 eV): *m*/*z* (%) = 624 ([M$^+$], 5), 622 ([M$^+$], 5), 551 (5), 549 (5), 490 (20), 488 (20), 117 (60), 73 (100), 59 (35).

HRMS (EI, 70 eV): *m*/*z* [M$^+$] calcd for $C_{24}H_{32}{}^{79}BrIO_6$: 622.0444; found: 622.0440.

UV/VIS (MeCN): λ_{max} (log ε) = 224 (4.32), 237 (4.31), 272 (sh, 4.33), 278 (sh, 4.36), 281 (4.42), 292 nm (4.40).

2-Bromo-3-iodo-1,4-bis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)benzene (17e)

Dibromide **7e** (1.68 g, 2.50 mmol) was subjected to the protocol for the synthesis of **17d**. Column chromatography (silica gel, EtOAc) begot **17e** as colorless crystals; yield: 1.52 g (85%); mp 102–103 °C (EtOH).

IR (KBr): 3068, 2986, 2875, 2823, 2221, 1602, 1570, 1516, 1491, 1471, 1457, 1450, 1382, 1364, 1353, 1342, 1331, 1303, 1280, 1250, 1196, 1166, 1145, 1123, 1101, 1061, 1028, 1006, 955, 936, 924, 903, 887, 855, 842, 827, 812, 787, 706, 644, 626, 536 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.8 Hz, 2 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 4.16 (m, 4 H), 3.87 (m, 4 H), 3.72 (m, 4 H), 3.58 (m, 4 H), 3.39 (s, 6 H).

^{1}H NMR (400 MHz, C_6D_6): δ = 7.53 (d, *J* = 8.8 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 7.02 (d, *J* = 8.0 Hz, 1 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 6.68 (d, *J* = 8.8 Hz, 2 H), 3.68 (m, 4 H), 3.51 (m, 4 H), 3.45 (m, 4 H), 3.33 (m, 4 H), 3.12 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 159.34, 159.31, 133.15, 133.04, 132.9, 131.7, 131.6, 129.7, 125.5, 114.67 (2 C), 114.65 (2 C), 108.7, 95.7, 95.1, 91.8, 88.1, 71.8 (2 C), 70.7 (2 C), 69.5 (2 C), 67.4 (2 C), 59.0 (2 C).

MS (EI, 70 eV): *m*/*z* (%) = 720 ([M$^+$], 80), 718 ([M$^+$], 80), 640 (5), 594 (20), 592 (20), 128 (10), 103 (20), 59 (100).

UV/VIS (MeCN): λ_{max} (log ε) = 222 (4.63), 241 (4.60), 346 (4.86), 363 nm (sh, 4.80).

1,4-Bis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}-2-iodo-3-[(trimethylsilyl)ethynyl]benzene (18d)

To **11d** (1.48 g, 2.50 mmol) in anhyd THF (100 mL) at –110 °C was added 1.6 M BuLi in hexane (1.9 mL, 3.0 mmol). After stirring for 1 h, I_2 (950 mg, 3.74 mmol) in anhyd THF (50 mL) was added dropwise via cannula. The mixture was stirred for an additional 30 min at –110 °C and then allowed to warm to r.t. The resulting solution was washed first with sat. aq $Na_2S_2O_3$, then H_2O, and dried ($MgSO_4$). The volatiles were removed in vacuo and the residue subjected to column chromatography (silica gel, Et_2O) to give **18d** as a light yellow oil; yield: 760 mg (47%).

IR (film): 2972, 2868, 2156, 1572, 1519, 1485, 1447, 1349, 1289, 1250, 1116, 1033, 971, 945, 882, 845, 761, 701, 681, 661, 623 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.0 Hz, 1 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 4.48 (s, 2 H), 4.47 (s, 2 H), 3.83 (m, 2 H), 3.77 (m, 2 H), 3.74–3.68 (m, 4 H), 3.68–3.63 (m, 4 H), 3.62–3.57 (m, 4 H), 3.518 (q, *J* = 7.0 Hz, 2 H), 3.513 (q, *J* = 7.0 Hz, 2 H), 1.199 (t, *J* = 7.0 Hz, 3 H), 1.194 (t, *J* = 7.0 Hz, 3 H), 0.27 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 132.7, 131.18, 131.14, 130.2, 125.6, 107.4, 105.3, 103.8, 91.3, 90.8, 88.3, 84.4, 70.65 (2 C), 70.63, 70.4, 69.74, 69.73, 69.29, 69.15, 66.6 (2 C), 59.01, 58.98, 15.11, 15.09, –0.30.

MS (EI, 70 eV): *m*/*z* (%) = 640 ([M$^+$], 30), 567 (10), 523 (10), 506 (25), 389 (10), 375 (117 (40), 103 (10), 73 (100), 59 (30).

HRMS (EI, 70 eV): *m*/*z* [M$^+$] calcd for $C_{29}H_{41}IO_6Si$: 640.1717; found: 640.1725.

UV/VIS (MeCN): λ_{max} (log ε) = 243 (sh, 4.41), 256 (sh, 4.57), 262 (4.63), 279 (4.32), 287 (4.29), 298 nm (4.35).

3-Iodo-1,4-bis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)-2-[(trimethylsilyl)ethynyl]benzene (18e)

Compound **11e** (1.73 g, 2.50 mmol) was reacted according to the procedure described for the synthesis of **18d** from **11d**. Column chromatography (silica gel, EtOAc) furnished **18e** as colorless needles; yield: 1.48 g (80%); mp 74–76 °C (MeOH).

IR (KBr): 2927, 2873, 2823, 2214, 2155, 1602, 1568, 1522, 1507, 1467, 1456, 1414, 1370, 1353, 1302, 1287, 1250, 1201, 1165, 1144, 1125, 1110, 1059, 1029, 968, 954, 936, 923, 843, 812, 761, 703, 671, 646, 618, 536 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.8 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 7.41 (d, *J* = 8.0 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 1 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 4.17 (m, 4 H), 3.88 (m, 4 H), 3.73 (m, 4 H), 3.58 (m, 4 H), 3.40 (s, 6 H), 0.31 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 159.26, 159.19, 133.15, 133.05, 132.3, 130.59, 130.54, 130.4, 125.9, 115.1, 114.9, 114.69, 114.62, 107.5, 105.8, 103.4, 95.7, 94.7, 91.2, 87.0, 71.9 (2 C), 70.7 (2 C), 69.6 (2 C), 67.4 (2 C), 59.0 (2 C), –0.21.

MS (EI, 70 eV): *m*/*z* (%) = 736 ([M$^+$], 90), 610 (100), 633 (5), 103 (10), 59 (60$^+$).

UV/VIS (MeCN): λ_{max} (log ε) = 236 (sh, 4.38), 258 (4.49), 273 (sh, 4.47), 345 (4.74), 361 nm (sh, 4.69).

3-Iodo-1,4-bis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)-2-[(triisopropylsilyl)ethynyl]benzene (19e)

Bromoarene **13e** (1.945 g, 2.50 mmol) was transformed following the procedure described for the synthesis of **18d** from **11d**. Column chromatography (silica gel, EtOAc) produced **19e** as light yellow needles; yield: 1.595 g (78%); mp 103–104 °C (EtOH).

IR (KBr): 2941, 2925, 2885, 2864, 2217, 2146, 1602, 1567, 1519, 1509, 1453, 1358, 1308, 1286, 1246, 1202, 1168, 1138, 1111, 1060, 1018, 996, 966, 950, 921, 883, 842, 831, 810, 770, 680, 647, 604, 537, 508 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.8 Hz, 2 H), 7.44 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 8.8 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 1 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 4.17 (m, 4 H), 3.87 (m, 4 H), 3.73 (m, 4 H), 3.59 (m, 4 H), 3.40 (s, 6 H), 1.15 (m, 21 H).

^{13}C NMR (100 MHz, $CDCl_3$, number of accidentally isochronous peaks based on relative peak heights or widths): δ = 159.2, 159.1, 133.2, 133.0, 132.2, 131.3, 131.0, 130.3, 126.1, 115.1, 115.0, 114.7, 114.4, 107.9, 107.1, 100.4, 95.3, 94.7, 91.2, 86.9, 71.9 (2 C), 70.7 (2 C), 69.58, 69.55, 67.4 (2 C), 59.0 (2 C), 18.7, 11.3.

MS (EI, 70 eV): *m*/*z* (%) = 820 ([M$^+$], 100), 694 (40), 103 (5), 59 (30).

HRMS (EI, 70 eV): *m*/*z* [M$^+$] calcd for $C_{43}H_{53}IO_6Si$: 820.2656; found: 820.2671.

UV/VIS (MeCN): λ_{max} (log ε) = 258 (4.63), 280 (4.61), 344 (4.76), 360 nm (sh, 4.68).

1,4-Bis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}-3-ethynyl-2-iodobenzene (20d)

To **18d** (1.28 g, 2.00 mmol) in MeOH (100 mL) was added sat. aq K_2CO_3 (1 mL, 8 mmol) at r.t. The resulting cloudy solution was stirred at r.t. until clear (30 min), diluted with CH_2Cl_2 (200 mL), washed with H_2O (3 × 100 mL), dried ($MgSO_4$), and the volatiles were removed under reduced pressure. Column chromatography (silica gel, Et_2O) resulted in **20d** as a heat- and light-sensitive, light yellow oil; yield: 1.12 g (99%).

IR (film): 3235, 2973, 2868, 2104, 1573, 1519, 1485, 1448, 1349, 1287, 1266, 1247, 1115, 1033, 971, 946, 839, 763, 748, 693, 670, 623 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.1 Hz, 1 H), 7.23 (d, *J* = 8.1 Hz, 1 H), 4.42 (s, 2 H), 4.41 (s, 2 H), 3.75 (m, 4 H), 3.69 (s, 1 H), 3.65 (m, 4 H), 3.60 (m, 4 H), 3.53 (m, 4 H), 3.45 (q, *J* = 7.0 Hz, 4 H), 1.139 (t, *J* = 7.0 Hz, 3 H), 1.135 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.7, 131.4, 131.0, 130.2, 126.1, 106.9, 91.5, 90.9, 88.1, 85.7, 84.12, 84.08, 70.49, 70.48, 70.24, 70.20, 69.60, 69.59, 69.2, 68.9, 66.41, 66.40, 58.84, 58.82, 14.98, 14.96.

MS (EI, 70 eV): *m*/*z* (%) = 568 ([M$^+$], 2), 495 (1), 434 (3), 377 (1), 277 (100), 262 (10), 209 (7), 201 (15), 199 (15), 183 (16), 149 (16), 117 (17), 103 (10), 73 (55), 59 (50).

HRMS (EI, 70 eV): *m*/*z* [M$^+$] calcd for $C_{26}H_{33}IO_6$: 568.1322; found: 568.1332.

UV/VIS (MeCN): λ_{max} (log ε) = 254 (4.50), 277 (4.30), 283 (4.31), 294 nm (4.43).

2-Ethynyl-3-iodo-1,4-bis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)benzene (20e) from 18e

Compound **18e** (1.47 g, 2.00 mmol) was converted according to the procedure described for the synthesis of **20d** from **18d**. Column chromatography (silica gel, EtOAc) presented **20e** as light yellow needles; yield: 1.27 g (96%); mp 88–90 °C (EtOH).

IR (KBr): 3246, 2940, 2927, 2878, 2828, 2809, 2216, 1602, 1569, 1519, 1508, 1490, 1471, 1456, 1356, 1333, 1303, 1287, 1249, 1195, 1168, 1139, 1121, 1098, 1062, 1030, 951, 937, 923, 852, 840, 827, 811, 792, 650, 614, 544, 534 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.8 Hz, 2 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 6.89 (ABq, 4 H), 4.15 (m, 4 H), 3.86 (m, 4 H), 3.71 (m, 4 H), 3.72 (s, 1 H), 3.60 (m, 4 H), 3.38 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.34, 159.31, 133.26, 133.1, 132.3, 131.0, 130.70, 130.5, 126.6, 114.94, 114.85, 114.73, 114.69, 107.2, 95.9, 95.0, 91.1, 86.8, 85.2, 84.7, 71.9 (2 C), 70.7 (2 C), 69.6 (2 C), 67.5 (2 C), 59.0 (2 C).

MS (EI, 70 eV): *m*/*z* (%) = 664 ([M$^+$], 75), 561 (3), 538 (9), 514 (6), 254 (10), 155 (20), 142 (70), 127 (50), 103 (10), 59 (100).

HRMS (EI, 70 eV): *m*/*z* [M$^+$] calcd for $C_{34}H_{33}IO_6$: 664.1322; found: 664.1332.

UV/VIS (MeCN): λ_{max} (log ε) = 257 (4.63), 344 (4.77), 354 (sh, 4.75), 362 nm (sh, 4.74).

2-Ethynyl-3-iodo-1,4-bis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)benzene (20e) from 19e

Compound **19e** (1.64 g, 2.00 mmol) in THF (75 mL) was subjected to 1 M TBAF in THF (2.20 mL, 2.20 mmol) at r.t. The solution, which turned yellow immediately, was stirred for 30 min (TLC monitoring), then diluted with CH_2Cl_2 (200 mL), washed with H_2O (3 × 100 mL), and dried ($MgSO_4$). After removal of the volatiles under reduced pressure, column chromatography (silica gel, EtOAc) afforded **20e**; yield: 1.29 g (97%).

1,4,7,10,13,16-Hexakis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-ynyl}tribenzo[*a*,*e*,*i*]cyclododeca-5,11,17-triyne (2d)

To CuCl (99 mg, 1.00 mmol) in aq NH_3 (60 mL) was added dropwise **20d** (568 mg, 1.00 mmol) in EtOH (60 mL). After stirring for 1 h at r.t., the resulting yellowish orange precipitate was collected by filtration, washed with H_2O, and dried under high vacuum overnight. The cuprate was dissolved in pyridine (75 mL) and the solution heated to reflux over a period of 6 h. After cooling to r.t., the volatiles were removed under reduced pressure, and the resulting dark brown residue was subjected to column chromatography (silica gel, Et_2O/THF 2:1) to supply **2d** as a yellow oil; yield: 104 mg (24%).

IR (film): 2971, 2917, 2868, 2223, 1467, 1375, 1348, 1287, 1247, 1104, 1032, 946, 840, 767, 734, 688, 633 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (s, 6 H, CH), 4.45 (s, 12 H), 3.74 (AA′m, 12 H), 3.65 (BB′m, 12 H), 3.61 (AA′m, 12 H), 3.55 (BB′m, 12 H), 3.49 (q, *J* = 7.0 Hz, 12 H), 1.18 (t, *J* = 7.0 Hz, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.5, 128.9, 125.6, 95.8, 91.8, 84.1, 70.5, 70.2, 69.6, 69.1, 66.5, 59.1, 15.0.

MS (FAB, 70 eV): *m*/*z* (%) = 1321.6 ([MH$^+$]).

UV/VIS (MeCN): λ_{max} (log ε) = 200 (4.55), 232 (sh, 4.41), 247 (4.60), 273 (4.70), 297 (4.68), 311 (4.64), 319 (4.59), 334 (4.81), 400 nm (2.96).

1,4,7,10,13,16-Hexakis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)tribenzo[*a*,*e*,*i*]cyclododeca-5,11,17-triyne (2e)

The recipe for the preparation of **2d** from **20d** was followed, except the solvent for **20e** (664 mg, 1.00 mmol) was EtOH/DMSO (1:2, 60 mL). Column chromatography (silica gel, EtOAc/acetone 4:1) sequestered **2e** as yellow crystals; yield: 122 mg (23%); mp 118–119 °C (EtOAc/hexane).

IR (KBr): 3069, 3042, 2923, 2876, 2823, 2198, 1604, 1567, 1511, 1462, 1417, 1356, 1288, 1250, 1199, 1169, 1139, 1127, 1109, 1059, 1028, 923, 830, 764, 627, 608, 535 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.39 (s, 6 H), 7.16 (d, *J* = 8.8 Hz, 12 H), 6.60 (d, *J* = 8.8 Hz, 12 H), 4.08 (AA′m, 12 H), 3.84 (BB′m, 12 H), 3.72 (AA′m, 12 H), 3.58 (BB′m, 12 H), 3.40 (s, 18 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6, 133.5, 131.8, 128.6, 126.1, 115.3, 113.9, 96.5, 96.5, 86.9, 71.9, 70.8, 69.7, 67.4, 59.1.

MS (FAB, 70 eV): *m*/*z* (%) = 1609.6 ([MH$^+$]).

HRMS (FAB): *m*/*z* [M$^+$] calcd for $C_{102}H_{96}O_{18}$: 1608.6597; found: 1608.6542.

UV/VIS (MeCN): λ_{max} (log ε) = 235 (sh, 4.51), 256 (4.80), 303 (sh, 4.75), 350 (5.20), 378 (sh, 4.99), 439 nm (3.69).

Fluorescence (MeCN, λ_{exc} = 350 nm): λ_{em} = 499 nm.

High Yield Preparation of 12d,e and 14e from 7d,e

(Trimethylsilyl)acetylene (1.14 mL, 786 mg, 8 mmol) or (triisopropylsilyl)acetylene (1.80 mL, 1.46 g, 8 mmol) in a Fisher–Porter bottle was injected in one portion into a mixture of the respective alkynylated 2,3-dibromobenzenes **7d**,**e** (2 mmol), $Cl_2Pd(PPh_3)_2$ (70 mg, 0.10 mmol), and CuI (19 mg, 0.10 mmol) in Et_3N (100 mL) at r.t. The vessel was sealed and the mixture stirred at 100 °C for 6 h. During this time the solution rapidly turned bright yellow, then yellow brown, and finally dark brown with the formation of a precipitate. After cooling to r.t., an additional portion of the silylalkyne (4 mmol) was added, the mixture stirred again at 100 °C for 6 h, allowed to cool to r.t., and filtered. The solvent was evaporated and the resulting residue purified by column chromatography (silica gel, Et_2O) to present, respectively, **12d** as a yellow oil; yield: 1.00 g (82%); **12e** as a yellow oil; yield: 1.10 g (78%); and **14e** as yellow crystals; yield: 1.00 g (57%).

1,4-Bis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}-2,3-diethynylbenzene (21d)

To **12d** (1.22 g, 2.00 mmol) in MeOH (100 mL) was added sat. aq K_2CO_3 (1 mL, 8 mmol) at r.t. The resulting cloudy solution was stirred until clear (30 min), diluted with CH_2Cl_2 (200 mL), washed with H_2O (3 × 100 mL), dried ($MgSO_4$), and the volatiles were removed under reduced pressure. Column chromatography (silica gel, Et_2O) resulted in **21d** as a heat- and light-sensitive, light yellow oil, stored at 0 °C; yield: 910 mg (98%).

IR (film): 3280, 3236, 2974, 2868, 2227, 2105, 1573, 1485, 1461, 1394, 1376, 1349, 1282, 1246, 1101, 1033, 946, 839, 642 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.34 (s, 2 H), 4.47 (s, 4 H), 3.81 (AA′m, 4 H), 3.70 (BB″m, 4 H), 3.65 (AA′m, 4 H), 3.61 (s, 2 H), 3.58 (BB′m, 4 H), 3.51 (q, *J* = 7.0 Hz, 4 H), 1.19 (t, *J* = 7.0 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.3, 127.6, 125.8, 91.3, 85.9, 83.9, 79.8, 70.5, 70.2, 69.6, 68.9, 66.4, 58.8, 15.0.

MS (FAB, 70 eV): *m*/*z* (%) = 467 ([MH$^+$]).

UV/VIS (MeCN): λ_{max} (log ε) = 247 (sh, 4.53), 253 (4.61), 257 (4.64), 277 (4.30), 283 (4.34), 294 nm (4.50).

2,3-Diethynyl-1,4-bis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}ethynyl)benzene (21e)

From **12e**: Compound **12e** (1.41 g, 2.00 mmol) was subjected to the reaction conditions used for the synthesis of **21d** from **12d**. Column chromatography (silica gel, EtOAc) gave **21e** as heat- and light-sensitive, light brown needles; yield: 1.04 g (92%); mp >50 °C dec (EtOH).

From **14e**: Compound **14e** (1.75 g, 2.00 mmol) in THF (75 mL) was exposed to 1 M TBAF in THF (2.2 mL, 2.2 mmol) at r.t. The solution turned yellow immediately and was stirred for 30 min. It was then diluted with CH_2Cl_2 (200 mL), washed with H_2O (3 × 100 mL), dried ($MgSO_4$), and the volatiles removed under reduced pressure. Work up of the residue as described above supplied **21e**; yield: 1.11 g (99%).

IR (KBr): 3261, 3073, 2927, 2882, 2829, 2208, 2109, 1602, 1512, 1467, 1450, 1356, 1290, 1252, 1203, 1174, 1163, 1138, 1110, 1057, 982, 949, 939, 923, 845, 828, 809, 769, 714, 664, 615, 533 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.8 Hz, 4 H), 7.44 (s, 2 H), 6.90 (d, *J* = 8.8 Hz, 4 H), 4.16 (AA′m, 4 H), 3.87 (BB′m, 4 H), 3.72 (AA′m, 4 H), 3.64 (s, 2 H), 3.58 (BB′m, 4 H), 3.39 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 133.3, 131.1, 127.4, 126.4, 115.0, 114.7, 95.7, 86.5, 85.4, 80.5, 71.9, 70.8, 69.6, 67.5, 59.0.

MS (FAB, 70 eV): *m*/*z* (%) = 562 ([M$^+$]).

UV/VIS (MeCN): λ_{max} (log ε) = 255 (4.52), 266 (sh, 4.46), 346 (4.67), 362 nm (sh, 4.62).

1,4,9,12-Tetrakis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}dibenzo[*a*,*g*]cyclododeca-5,7,13,15-tetrayne (4a) and 1,4,9,12,17,20-Hexakis{3-[2-(2-ethoxyethoxy)ethoxy]prop-1-yn-1-yl}tribenzo[*a*,*g*,*m*]cyclooctadeca-5,7,13,15,21,23-hexayne (22d)

Through a solution of **21d** (933 mg, 2.00 mmol) and CuCl (238 mg, 2.40 mmol) in chlorobenzene (125 mL) was passed a continuous stream of dry O_2 for 15 min to ensure saturation. TMEDA (10 mL) was then added dropwise under vigorous stirring at r.t. The mixture immediately turned yellow, then green, and finally cloudy dark green with the formation of a precipitate upon completion of the addition. After stirring for an additional 1 h under O_2, the reaction was quenched with 1 M aq HCl (100 mL), CH_2Cl_2 (100 mL) added, the mixture shaken, the organic layer collected, and the aqueous layer further extracted with CH_2Cl_2 (5 × 100 mL). The combined organic phases were washed with sat. aq $NaHCO_3$ and then H_2O. The volatiles were removed under reduced pressure and the resulting solid yellow brown residue was subjected to column chromatography (silica gel, Et_2O/THF 5:1), leading to a first fraction containing air-sensitive **4a** forming golden plates; yield: 360 mg (39%); mp 104–105 °C dec (CH_2Cl_2/hexane).

IR (KBr): 2973, 2911, 2869, 2222, 2121, 1480, 1456, 1443, 1375, 1346, 1289, 1261, 1245, 1118, 1099, 1088, 1029, 951, 852, 835, 664, 626 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.06 (s, 4 H), 4.42 (s, 8 H), 3.73 (AA′m, 8 H), 3.69 (BB′m, 8 H), 3.65 (AA′m, 8 H), 3.60 (BB′m, 8 H), 3.52 (q, *J* = 7.0 Hz, 8 H), 1.20 (t, *J* = 7.0 Hz, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.3, 132.3, 122.8, 91.9, 91.6, 87.3, 83.2, 70.6, 70.3, 69.7, 69.2, 66.5, 58.9, 15.1.

MS (FAB, 70 eV): *m*/*z* (%) = 929.5 ([MH$^+$]).

HRMS (FAB, 70 eV): *m*/*z* [MH$^+$] calcd for $C_{56}H_{65}O_{12}$: 929.4476; found: 929.4480.

UV/VIS (MeCN): λ_{max} (log ε) = 212 (4.68), 245 (sh, 4.70), 250 (4.77), 275 (sh, 4.64), 280 (sh, 4.70), 286 (4.81), 295 (sh, 4.63), 302 (sh, 4.51), 317 (4.77), 324 (4.57), 327 (sh, 4.54), 339 (5.06), 420 nm (3.94).

Fluorescence (MeCN, λ_{exc} = 340 nm): λ_{em} = 501, 539, 548 nm.

On switching the chromatography solvent to Et_2O/THF (2:1), a second fraction emerged containing **22d** as a yellow oil; yield: 36 mg (4%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (s, 6 H), 4.55 (s, 12 H), 3.85 (AA′m, 12 H), 3.73 (BB′m, 12 H), 3.64 (AA′m, 12 H), 3.58 (BB′m, 12 H), 3.49 (q, *J* = 7.0 Hz, 12 H), 1.18 (t, *J* = 7.0 Hz, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.1, 127.5, 126.6, 92.6, 83.8, 82.0, 80.3, 70.6, 70.4, 69.8, 69.2, 66.6, 59.1, 15.1.

1,4,9,12-Tetrakis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}-ethynyl)dibenzo[*a*,*g*]cyclododeca-5,7,13,15-tetrayne (4b) and 1,4,9,12,17,20-Hexakis({4-[2-(2-methoxyethoxy)ethoxy]phenyl}-ethynyl)tribenzo[*a*,*g*,*m*]cyclooctadeca-5,7,13,15,21,23-hexayne (22e)

Following the procedure executed for the synthesis of **4a** and **22d**, oxidative coupling of **21e** (1.12 g, 2.00 mmol), followed by column chromatography (silica gel, EtOAc/acetone 4:1), afforded first **4b** as air-sensitive yellow crystals; yield: 270 mg (24%); mp 30–40 °C dec (toluene).

IR (KBr): 3070, 3044, 2925, 2876, 2823, 2211, 1604, 1570, 1514, 1474, 1453, 1355, 1285, 1250, 1199, 1167, 1130, 1110, 1059, 923, 827, 649, 605, 535, 487 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.8 Hz, 8 H), 7.13 (s, 4 H), 6.89 (d, *J* = 8.8 Hz, 8 H), 4.17 (AA′m, 8 H), 3.88 (BB′m, 8 H), 3.73 (AA′m, 8 H), 3.58 (BB′m, 8 H), 3.39 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 133.5, 132.9, 132.1, 123.3, 114.73, 114.67, 96.0, 92.1, 87.5, 85.9, 72.0, 70.8, 69.7, 67.5, 59.1.

MS (FAB, 70 eV): *m*/*z* (%) = 1120.6 ([M$^+$]).

HRMS (FAB, 70 eV): *m*/*z* [M$^+$] calcd for $C_{72}H_{64}O_{12}$: 1120.4398; found: 1120.4408.

UV/VIS (MeCN): λ_{max} (log ε) = 248 (sh, 4.77), 255 (4.84), 346 (5.05), 367 (5.02), 457 nm (3.94).

Fluorescence (MeCN, λ_{exc} = 365 nm): λ_{em} = 502, 545, 555 nm.

A second fraction contained waxy, impure **22e**, characterized solely by a ^{1}H NMR spectrum; (maximum) yield: 16 mg (1.4%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (s, 6 H), 7.35 (d, *J* = 8.8 Hz, 12 H), 6.56 (d, *J* = 8.8 Hz, 12 H), 3.98 (m, 12 H), 3.82 (m, 12 H), 3.72 (m, 12 H), 3.59 (m, 12 H), 3.41 (s, 18 H).

Cobalt-Catalyzed Cycloisomerization of 2e to 23

To boiling *m*-xylene (120 mL) was added **2e** (120 mg, 0.075 mmol) and $CpCo(CO)_2$ (33 µL, 45 mg, 0.25 mmol) in *m*-xylene (30 mL) in one portion. The mixture was maintained at reflux for 25 min, while being irradiated with a 300 W slide projector lamp at 60 V. During this time, the solution turned deep red exhibiting a yellow fluorescence. After removal of the solvent under vacuum, the residue was subjected to column chromatography (silica gel, EtOAc/acetone 3:1) to give **23** as a red solid; yield: 72 mg (60%).

IR (KBr): 2923, 2875, 2824, 2197, 1605, 1511, 1453, 1355, 1287, 1250, 1171, 1128, 1110, 1061, 934, 925, 830, 534 cm^{-1}.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.36 (s, 2 H), 7.20 (d, *J* = 8.6 Hz, 4 H), 7.15 (d, *J* = 8.6 Hz, 4 H), 7.10 (d, *J* = 7.4 Hz, 2 H), 7.06 (d, *J* = 8.6 Hz, 4 H), 6.80 (d, *J* = 8.6 Hz, 4 H), 6.62 (d, *J* = 7.4 Hz, 2 H), 6.60 (ABq, 8 H), 4.08 (m, 4 H), 4.04 (m, 8 H), 3.80 (m, 12 H), 3.66 (m, 12 H), 3.54 (m, 12 H), 3.36 (s, 12 H), 3.35 (s, 6 H).

^{13}C NMR (125 MHz, CD_2Cl_2): δ = 159.4, 159.2, 158.8, 151.9, 149.8, 147.1, 134.7, 134.2, 133.9, 132.5, 130.7, 130.6, 129.2, 128.9, 126.6, 125.9, 118.4 (2 C), 116.7, 116.0, 115.7, 114.6, 114.5, 114.4, 97.4, 95.5, 94.9, 94.1, 88.2, 87.4, 72.5 (3 C), 71.24 (2 C), 71.20, 70.20, 70.12, 70.11, 68.10, 68.08, 68.04, 59.3 (3 C).

MS (FAB, 70 eV): *m*/*z* (%) = 1609.9 ([MH$^+$]).

HRMS (FAB, 70 eV): *m*/*z* [M$^+$] calcd for $C_{102}H_{96}O_{18}$: 1608.6597; found: 1608.6622.

UV/VIS (MeCN): λ_{max} (log ε) = 261 (5.16), 309 (5.18), 344 (5.32), 422 (4.64), 441 (sh, 4.59), 465 (sh, 4.40), 538 nm (3.78).

Fluorescence (MeCN, λ_{exc} = 350 nm): λ_{em} = 568 nm.

Cobalt-Catalyzed Cycloisomerization of 23 to 24

Angular [3]phenylene derivative **23** (56 mg, 0.035 mmol) and $CpCo(CO)_2$ (33 µL, 45 mg, 0.25 mmol) in tetraglyme (30 mL) were added in one portion to boiling tetraglyme (120 mL). The mixture was maintained at reflux for 25 min, while being irradiated with a 300 W projector lamp at 60 V. During this time, the solution turned deep red possessing an orange fluorescence. After removal of the solvent under vacuum, the residue was subjected to column chromatography (silica gel, EtOAc/acetone 3:1) to give **24** as a deep red solid; yield: 12 mg (21%).

IR (KBr): 2924, 2855, 2203, 1606, 1511, 1455, 1384, 1355, 1286, 1250, 1199, 1178, 1109, 1063, 927, 825 cm^{-1}.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.12 (d, *J* = 8.8 Hz, 4 H), 6.94 (d, *J* = 8.8 Hz, 4 H), 6.93 (d, *J* = 8.8 Hz, 4 H), 6.90 (d, *J* = 7.3 Hz, 2 H), 6.73 (d, *J* = 8.8 Hz, 4 H), 6.69 (d, *J* = 8.8 Hz, 4 H), 6.52 (d, *J* = 8.8 Hz, 4 H), 6.40 (d, *J* = 7.3 Hz, 2 H), 6.18 (s, 2 H), 4.08 (m, 8 H), 4.00 (m, 4 H), 3.80 (m, 12 H), 3.66 (m, 12 H), 3.54 (m, 12 H), 3.357 (s, 6 H), 3.354 (s, 6 H), 3.349 (s, 6 H).

MS (FAB, 70 eV): *m*/*z* (%) = 1609.8 ([MH$^+$]).

HRMS (FAB, 70 eV): *m*/*z* [M$^+$] calcd for $C_{102}H_{96}O_{18}$: 1608.6597; found: 1608.6598.

UV/VIS (MeCN): λ_{max} (A) = 282 (0.44), 296 (sh, 0.40), 347 (0.31), 396 (sh, 0.15), 487 (0.02), 525 (sh, 0.01), 583 nm (0.01).

Fluorescence (MeCN, λ_{exc} = 350 nm): λ_{em} = 594 nm.

3,6,9,16,19,22-Hexaoxatetracosa-11,13-diyne (5a)

Through a solution of **6a** (1.72 g, 10 mmol) and CuCl (119 mg, 1.20 mmol) in acetone (75 mL) was passed a continuous stream of dry O_2 for 15 min to ensure saturation. TMEDA (1 mL) was then added in one portion under vigorous stirring at r.t. The mixture immediately turned green and then dark green with the formation of a precipitate. After stirring for an additional 4 h under O_2, the reaction was quenched with 1 M aq HCl (75 mL), CH_2Cl_2 (100 mL) added, the mixture shaken, the organic layer collected, and the aqueous layer further extracted with CH_2Cl_2 (5 × 100 mL). The combined organic phases were washed with sat. aq $NaHCO_3$, then H_2O, and finally dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the resulting solid yellow brown residue was subjected to column chromatography (silica gel, Et_2O) to provide **5a** as a light-sensitive, light yellow oil; yield: 1.41 g (82%).

IR (film): 2974, 2869, 2253, 2177, 2120, 1486, 1457, 1443, 1376, 1348, 1290, 1246, 1093, 1030, 999, 945, 921, 844 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.27 (s, 4 H), 3.68 (m, 8 H), 3.65 (AA′m, 4 H), 3.60 (BB′m, 4 H), 3.52 (q, *J* = 7.0 Hz, 4 H), 1.21 (t, *J* = 7.0 Hz, 6 H).

^{13}C NMR (100 MHz, C_6D_6): δ = 76.8, 71.4, 71.2, 71.1, 70.7, 70.1, 67.0, 59.1, 15.8.

MS (FAB, 70 eV): *m*/*z* (%) = 343.2 ([MH$^+$]).

HRMS (FAB, 70 eV): *m*/*z* [MH$^+$] calcd for $C_{18}H_{31}O_6$: 343.2121; found: 343.2119.

1,4-Bis{4-[2-(2-methoxyethoxy)ethoxy]phenyl}buta-1,3-diyne (5b)

In a replication of the manner in which **5a** was assembled, **6b** (2.20 g, 10 mmol) was subjected to oxidative coupling and purified by column chromatography (silica gel, EtOAc) to create **5b** as colorless crystals; yield: 1.98 g (90%); mp 84–85 °C (EtOH).

IR (KBr): 3074, 3045, 2971, 2943, 2913, 2878, 2140, 1639, 1599, 1504, 1466, 1451, 1399, 1380, 1357, 1307, 1285, 1248, 1201, 1171, 1141, 1120, 1079, 1058, 1032, 960, 953, 942, 923, 851, 829, 721, 640, 574, 537, 456 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 6.0 Hz, 4 H), 6.86 (d, *J* = 6.0 Hz, 4 H), 4.15 (AA′m, 4 H), 3.86 (BB′m, 4 H), 3.71 (AA′m, 4 H), 3.57 (BB′m, 4 H), 3.39 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 133.9, 114.7, 113.9, 81.1, 72.9, 71.8, 70.6, 69.5, 67.4, 58.9.

MS (FAB, 70 eV): *m*/*z* (%) = 438 ([M$^+$]).

UV/VIS (MeCN): λ_{max} (log ε) = 203 (4.74), 242 (sh, 4.28), 260 (sh, 4.41), 268 (4.47), 281 (4.50), 299 (4.56), 319 (4.65), 340 nm (3.54).

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Supporting Information

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