Monodisperse Oligo(2,5-dipropoxy-1,4-phenyleneethynylene)s

Dirk Ickenroth,[a] Silke Weissmann,[a] Norbert Rumpf,[a] and Herbert Meier*[a]

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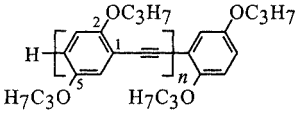
Oligo(phenyleneethynylene)s **1** are rod-like compounds with undisturbed conjugation. In supplementation of the previously described members of this series **1a–e**, with repeating units of up to $n = 5$, this work contains the preparation of higher oligomers **1f–i** ($n = 6, 7, 8, 10$) through the use of the Sonogashira–Hagihara reaction. Both the absorption and the fluorescence bands showed convergence for increasing values of n, reaching limiting values at the effective conjugation length of $n_{ECL} = 10$.

Introduction

Conjugated oligomers represent interesting compounds for many applications in materials science.[1−31] Moreover, their properties as − for example − electrical semiconductors, photoconductors, electroluminophores, and materials for nonlinear optics (NLO) make them model compounds for the corresponding conjugated polymers, which have compared to the oligomers some advantages in processing. In this context we decided to synthesize a series of monodisperse oligo(2,5-dipropoxy-1,4-phenyleneethynylene)s (OPEs) **1a**−**i**. The first five members of the series (n = 1−5) and their astonishingly high second order hyperpolarizabilities γ were described recently.[31] We have now extended the study to the convergence of the electronic properties for $n \rightarrow \infty$: that means, to the ideal, defect-free polymer.



1	a	b	c	d	e	f	g	h	i
n	1	2	3	4	5	6	7	8	10

Scheme 1. Oligo(2,5-dipropoxy-1,4-phenyleneethynylene)s (OPEs) **1a**−**i**

Propoxy chains confer sufficient solubility and processability. Moreover, they shift the absorption and the fluorescence to longer wavelengths.

[a] Institut für Organische Chemie der Johannes Gutenberg-Universität Mainz,
Duesbergweg 10−14, 55099 Mainz, Germany
Fax: (internat.) +49-(0)6131/3925396
E-mail: hmeier@mail.uni-mainz.de

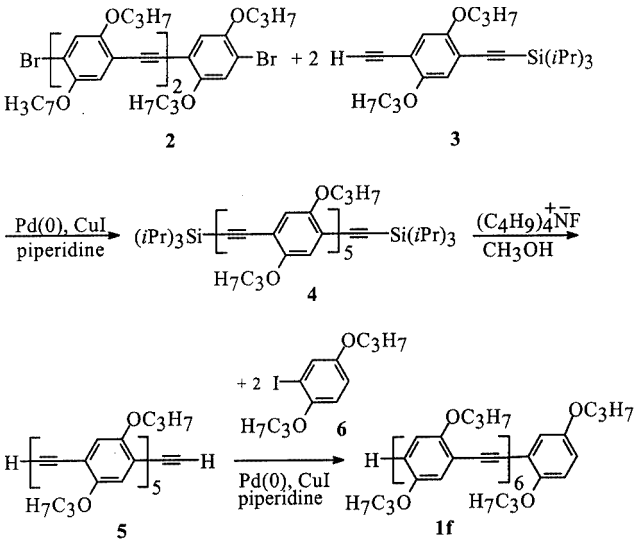
Results and Discussion

In the previous paper,[31] which dealt with the preparation of the OPEs **1a**−**e**, the synthetic strategy was based on Sonogashira−Hagihara reactions between iodo- or bromoarenes and ethynylarenes. Important features of the Pd^0-catalyzed $C(sp^2)-C(sp)$ coupling reactions were the higher reactivity of the iodo compounds relative to the bromo compounds and a selective protecting group technique on the ethynyl side. A set of building blocks serving for the preparation of **1a**−**e** was thus obtained, and this starter kit could now be applied for the formation of the higher oligomers **1f**−**i**.

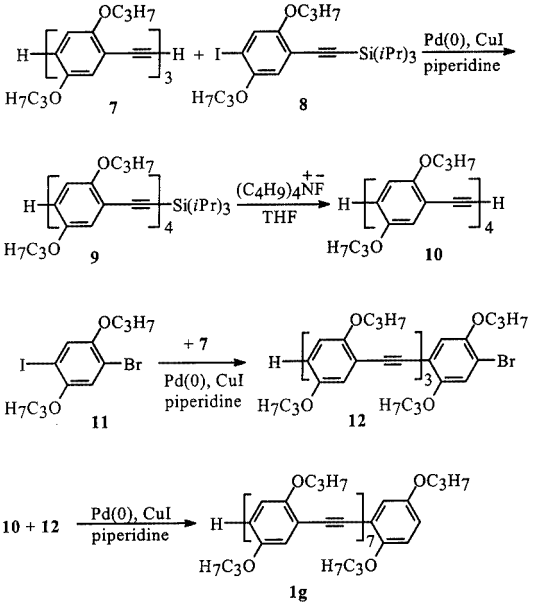
The preparation of the hexamer **1f** made use of the dibromo compound **2** and the half-protected diethynyl compound **3**. In a double coupling reaction, the pentamer **4** with two triisopropylsilyl end groups was obtained. Deprotection with tetrabutylammonium fluoride provided the pentamer **5**, which, on coupling with the iodobenzene **6** on both sides, gave OPE **1f**.

The preparation of the heptamer **1g** began with the trimer **7**. Coupling with the iodo compound **8** yielded the tetramer **9**, which was deprotected to afford the ethynyl system **10**. In addition, **7** was coupled with **11** to give the trimer **12**. The bromo substituent was maintained intact under the mild conditions and could then be used for the final coupling **10** + **12** → **1g**.

Scheme 4 illustrates the production of the octamer **1h** and the decamer **1i**. The dibromo compound **13** was coupled with two equivalents of the trimer **7** and gave OPE **1h**, while the diiodo compound **15** furnished OPE **1i** through coupling with the pentamer **14**. The yields obtained in Sonogashira−Hagihara reactions tend to be lower with bromo components than with iodo compounds, because the reaction rate with bromoarenes is lower and side reactions can take place. One especially has to take care to ensure oxygen-free reaction media, so that the competing



Scheme 2. Synthesis of the hexamer OPE **1f**

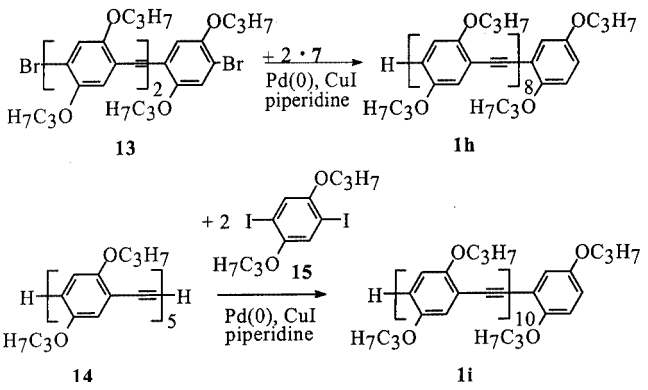


Scheme 3. Synthesis of the heptamer OPE **1g**

oxidative coupling is reduced to a minimum (this cannot be completely avoided because of the presence of Pd^{II}).

The NMR spectroscopic characterization of the oligomers **1a**−**i** revealed that the terminal benzene rings − irrespective of the number of repeat units *n* − gave signals that could be distinguished from the signals of the inner segments. A pronounced anisotropy effect in the inner parts of the rigid conjugated chain gave rise to low-field shifts for the aromatic protons, the aromatic methine carbon atoms, and for the acetylenic carbon atoms. Table 1 summarizes the NMR spectroscopic data of the compounds **1a**−**i**.

The field desorption technique proved suitable for mass spectrometry of the oligomers **1a**−**i**. In addition to the (protonated) molecular ions M^+, the M^{2+} peaks could be found



Scheme 4. Synthesis of octamer OPE **1h** and decamer OPE **1i**

for all members of the series. Moreover, more highly charged ions M^{3+}, M^{4+}, etc. were also detected for the longer chains ($n \geq 4$). The short systems **1a**−**d** showed additional peaks $[2\ M]^+$ of dimeric aggregates.

Because of the symmetry of the molecules, the FT−IR spectra of the oligomers **1a**−**i** did not exhibit CC triple bond stretching vibrations. The most intense bands were found at (1509 ± 7) cm^{-1} for the aromatic stretching vibrations, at (1432 ± 5) cm^{-1} for the CH_2 deformation vibrations, and at (1273 ± 3) cm^{-1} and (1210 ± 8) cm^{-1} for the stretching vibrations of the CO single bonds.

The most important spectroscopic characterization of the oligomers **1a**−**i** concerned UV/Vis and fluorescence spectroscopy. Unlike the IR and NMR spectra, which both predominantly reflected the data for the repeating units, the electronic spectra depended on the length of the chromophores. Since there were no special steric or push-pull effects[32] present in **1a**−**i**, a monotonous bathochromic shift of the absorption and fluorescence bands with increasing *n* was to be expected. The convergence of the energies *E*(*n*) of the electronic transitions for $n \rightarrow \infty$ can be quantitatively described by exponential functions.[33] Apart from the validity for the $0 \rightarrow 0$ transitions, the absorption and fluorescence maxima can be taken in the majority of conjugated series.[33] If the vibrational structure does not allow the $0 \rightarrow 0$ transitions to be determined, one can also use the absorption edges $\lambda_{0.1}$, where ε is 1/10 of ε_{max}. Table 2 summarizes the absorption and emission data of the oligomers **1a**−**i**.

The λ_{max} values of the UV/Vis absorption bands of **1a**−**i** at most depended only to a very small extent on the concentrations of the solutions in $CHCl_3$. Such dependence was observed for *n* = 4, 5, and 6. We attributed this result to aggregation, and compared it to the strong influence of concentration on the fluorescence spectra. Figure 1 depicts three selected examples: the emissions of **1b** (*n* = 2, λ_{exc} = 378 nm), **1d** (*n* = 4, λ_{exc} = 412 nm), and **1h** (*n* = 8, λ_{exc} = 435 nm). Each spectrum showed two different bands, the ratio of the intensities of the two bands changing markedly with the concentration. The broad bands at longer wavelengths decreased with decreasing concentration; we there-

Table 1. $^1H/^{13}C$ NMR spectroscopic data of the oligomer OPEs **1a−i** (δ values in $CDCl_3$, TMS as internal standard)

Group	Position in the chain	
	Terminal phenylethynyl segment	Inner phenylene-ethynylene segment
H_2CO-C-2	3.97 ± 0.10/71.3 ± 0.2	3.97 ± 0.10/71.3 ± 0.2
H_2CO-C-5	3.86 ± 0.01/70.2 ± 0.1	3.97 ± 0.10/71.3 ± 0.2
HC-3	6.81 ± 0.01/114.4 ± 0.3	7.01 ± 0.03/117.7 ± 0.8
HC-4	6.81 ± 0.01/116.6 ± 0.3	−/−
HC-6	7.01 ± 0.03/118.5 ± 0.3	7.01 ± 0.03/117.7 ± 0.8
C_q	−/114.3 ± 0.2	−/114.5 ± 0.4
C_qO	−/152.9 ± 0.3	−/153.5 ± 0.3
	−/154.3 ± 0.3	−/153.5 ± 0.3
C(sp)	−/89.8 ± 0.2	−/91.5 ± 0.3

Table 2. Oligo(1,4-phenyleneethynylene)s **1a−i**

1	Repeating units n	Absorption in $CHCl_3$ λ_{max} [nm]	$\lambda_{0.1}$ [nm]	10^{-3} ε_{max} [a] [L·mol^{-1}·cm^{-1}]	Fluorescence in $CHCl_3$ [b] λ_{max} [nm]	Absorption in polystyrene λ_{max} [nm]
a	1	338	367	15.9	371	335
b	2	378	410	39.0	411	377
c	3	399	436	54.7	437	394
d	4	412	452	80.6	453	410
e	5	419	460	112.1	462	417
f	6	424	466	132.0	466	423
g	7	430	469	156.2	469	427
h	8	434	471	180.0	471	430
i	10	438	475	202.2	475	−

[a] The average ε_{max}/n amounts to $20.35 \cdot 10^3$ L·mol^{-1}·cm^{-1}. [b] The excitation wavelengths used for the fluorescence measurements corresponded to the absorption maxima (λ_{max} ± 1.0) nm.

fore attributed this emission to an aggregate. (The other compounds of the **1** series displayed the same behavior.) For compound **1d**, the maximum of the aggregate emission was higher than the maximum of the monomer emission even in the 10^{-4} M solution. Lowering of the concentration to 10^{-5} M and 10^{-6} M resulted here − as in all other cases − in an intensity decrease. The effect was more pronounced for the higher oligomers such as **1h** than for the lower oligomers.

How is it possible to explain the fact that absorption did not show a concentration effect − except for some medium oligomers (n = 4, 5, 6) − while fluorescence displayed very strong dependence on the concentration for all oligomers **1a−i**?

Either the strong aggregation tendency could be present only in the first excited singlet state S_1, so that we would see a kind of excimer fluorescence, or the aggregates could also be formed in the ground state S_0, but the geometrical arrangement might be such that monomer absorption and aggregate absorption would differ either not at all or very little. The latter precondition would be ideally fulfilled for an arrangement between J and H aggregation with parallel but laterally shifted chains in the so-called "magic angle" arrangement. The average lifetime of the S_1 states would certainly be sufficient for a geometrical change resulting in a different emission.

Nevertheless, all λ_{max} values of the absorption and the fluorescence bands could be used for the determination of the convergence ($n \rightarrow \infty$). Figure 2 shows the corresponding plots based on exponential functions:[33]

$$\lambda(n) = \lambda_\infty - (\lambda_\infty - \lambda_1)e^{-b(n-1)} \quad (1)$$

Table 3 summarizes the values for the fit to parameter b, the extrapolated wavelength λ_∞, the total effect of conjugation[33]

$$\Delta E = hc\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_\infty}\right) \quad (2)$$

and the effective conjugation length

$$n_{ECL} = \frac{\ln(\lambda_\infty - \lambda_1)}{b} + 1 \quad (3)$$

It turned out that **1i** (n = 10) just reached the convergence limits both of the absorption and of the fluorescence. The total effect of conjugation ΔE gave an answer to the question of how much the absorption and the fluorescence would be shifted on going from the very first member of the series (**1a**) to the infinitely long chain. The values for n_{ECL} and ΔE in the OPE series **1** were somewhat smaller

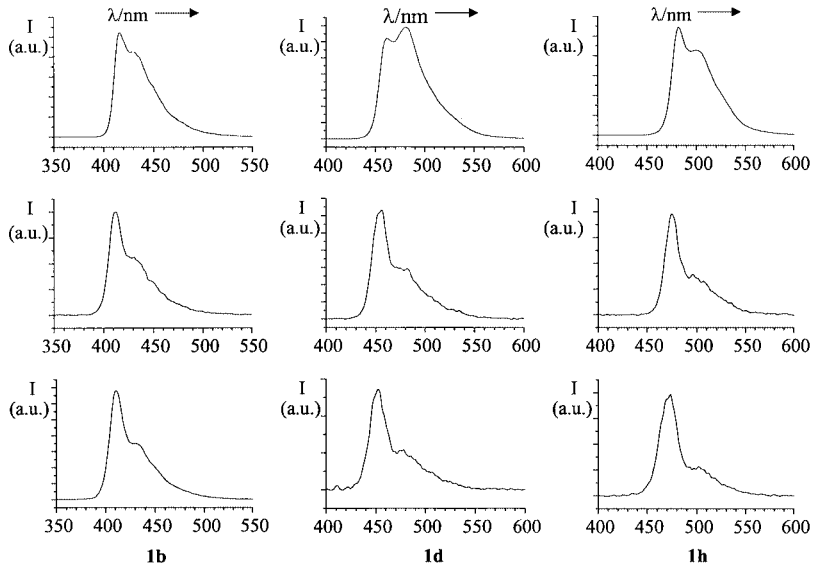


Figure 1. Fluorescence spectra (uncorrected) of **1b**, **1d**, and **1h** in $CHCl_3$; concentration: top 10^{-4} M, middle 10^{-5} M, bottom 10^{-6} M

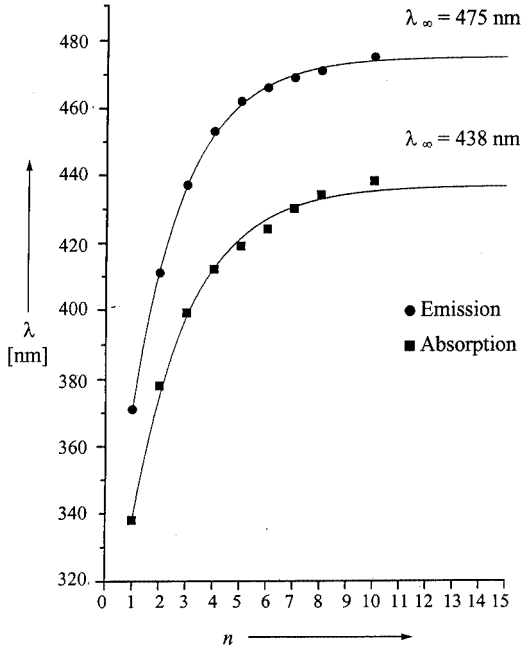


Figure 2. Convergence of the λ_{max} values of the absorption and the fluorescence for increasing numbers n of repeat units in the series **1** measured in $CHCl_3$. (The exponential fit function (1) is specified by the parameters given in Table 3.)

Table 3. Convergence data of the long-wavelength absorption and the monomer emission of **1a**−**i**

	Absorption	Fluorescence
b	0.468 ± 0.027	0.502 ± 0.012
λ_∞ [nm]	438 ± 3	475 ± 3
$(\lambda_\infty - \lambda_1)$ [nm]	100 ± 3	104 ± 3
ΔE [eV]	0.837	0.732
n_{ECL}	10	10

than those found in the series of the oligo(2,5-dipropoxyphenylenevinylene)s, with *trans* configured double bonds instead of the triple bonds.[33] Although steric hindrance caused torsions along the chain in the OPV series, impairing the conjugation, the effect of conjugation was higher for the olefinic systems. This result can be explained by the resonance integrals, which were less different in the OPV series because the bond lengths were less different than in the OPE series.

Summary and Conclusions

In supplementation of the previously described oligo(2,5-dipropoxy-1,4-phenyleneethynylene)s **1a**−**e** (n = 1−5),[31] we report here on the preparation of the higher members **1f**−**i** (n = 6−8, 10) of the OPE series. The monotonous bathochromic shifts of the absorption and fluorescence maxima of the whole series **1a**−**i** now permit the extrapolation ($n \rightarrow \infty$), giving limiting values λ_∞ of 438 and 475 nm, respectively. The effective conjugation length was reached for n_{ECL} = 10. Longer defect-free segments of polymer chains PPE would not change the extrapolated values unless special end groups were present.[32] Whereas the absorption spectra of **1a**−**i** in chloroform were independent of concentration − with slight exceptions for n = 4−6 − the fluorescence spectra exhibited, together with the monomer bands, second bands at longer wavelengths, the intensities of which decreased with decreasing concentration and were therefore attributed to aggregate emission (excimer emission).

Experimental Section

General: Melting points (uncorrected): Büchi apparatus. NMR: Bruker AM 400 and ARX 400, $CDCl_3$ as solvent unless otherwise

stated, TMS as internal standard. MS: Varian MAT CH7A and Finnigan MAT 95. UV/Vis: Zeiss MCS 320/340 and Perkin−Elmer Lambda 20, chloroform as solvent. Fluorescence: Perkin−Elmer LS 50 B (chloroform). FT-IR: Perkin−Elmer GX, KBr pellets.

1,4-Bis{2,5-dipropoxy-4-[2,5-dipropoxy-4-(triisopropylsilylethynyl)-phenylethynyl]phenylethynyl}-2,5-dipropoxybenzene (4): Triphenylphosphane (0.10 g, 0.38 mmol), CuI (0.07 g, 0.38 mmol), and $Pd(PPh_3)_2Cl_2$ (0.13 g, 0.19 mmol) were added to a degassed solution of **2**[31] (3.0 g, 3.82 mmol) and **3**[31] (3.6 g, 9.03 mmol) in 100 mL of toluene/50 mL of piperidine. After the mixture had been stirred for 16 h under nitrogen, the solvent was removed, and the residue was dissolved in 100 mL of CH_2Cl_2, washed with 50 mL of NH_4Cl, 50 mL of water, and 50 mL of $NaHCO_3$, and dried over Na_2SO_4. Column chromatography (30 × 3 cm SiO_2, toluene) yielded yellow crystals (2.1 g, 39%), which melted at 195 °C. ^{1}H NMR ($CDCl_3$): δ = 1.06 (m, 72 H, CH_3 and CH and CH_3 of $Si[CH(CH_3)_2]_3$), 1.82 (m, 20 H, CH_2), 3.94 (m, 20 H, OCH_2), 6.92/6.94 (2 s, 2 H and 2 H, arom. H of outer benzene rings), 7.00 (s, 6 H, arom. H of inner benzene rings) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.4 (CH_3), 11.3 (CH of isopropyl), 18.6 (CH_3 of isopropyl), 22.6, 22.7 (CH_2), 70.9, 71.2, 71.4 (OCH_2), 91.3, 91.5, 96.4, 103.0 (acetyl. C), 114.1, 114.4, 116.8, 117.5, 118.1 (arom. C), 153.2, 153.5, 154.3 (C_qO) ppm.[34] MS (FD): *m/z* (%) = 1421 $[M + H]^+$, 711 $[M + H]^{2+}$, 474 (1) $[M + H]^{3+}$. $C_{90}H_{122}O_{10}Si_2$ (1420.1): calcd. C 76.12, H 8.66; found C 76.08, H 8.63.

1,4-Bis{2,5-dipropoxy-4-[2,5-dipropoxy-4-(ethynyl)phenylethynyl]-phenylethynyl}-2,5-dipropoxybenzene (5): Compound **4** (0.56 g, 0.39 mmol) was dissolved in THF (25 mL) and treated with $(C_4H_9)_4N^+F$ (0.19 g, 0.59 mmol). After 15 min the solvent was removed, and the residue was dissolved in 50 mL of CH_2Cl_2 and extracted with 50 mL of water. The organic phase was dried with Na_2SO_4, concentrated, and purified by column chromatography (30 × 3 cm SiO_2, CH_2Cl_2). Yellow crystals (0.44 g, 96%) were obtained, and these melted at 173 °C. ^{1}H NMR ($CDCl_3$): δ = 1.07 (m, 30 H, CH_3), 1.83 (m, 20 H, CH_2), 3.33 (s, 2 H, acetyl. H), 3.97 (m, 20 H, OCH_2), 6.96/6.98 (2 s, 2 H and 2 H, arom. H of the outer benzene rings), 7.00 (s, 6 H, arom. H of the inner benzene rings) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.4, 10.5 (CH_3), 22.6, 22.7 (CH_2), 71.2, 71.3, 71.4 (OCH_2), 91.3, 91.6, 91.7 (acetyl. C), 112.9, 114.4, 114.6, 114.7, 115.3, 117.4, 117.7, 118.3 (arom. C), 153.5, 153.6, 154.3 (C_qO) ppm.[34] MS (FD): *m/z* (%) = 1107 (100) $[M]^+$, 554 (36) $[M]^{2+}$. $C_{72}H_{82}O_{10}$ (1107.4): calcd. C 78.09, H 7.46; found C 77.95, H 7.51.

Hexamer OPE 1f: Triphenylphosphane (15 mg, 0.057 mmol), CuI (11 mg, 0.057 mmol), and $Pd(PPh_3)_2Cl_2$ (20 mg, 0.029 mmol) were added to a degassed solution of **5** (300 mg, 0.27 mmol) and **6**[31] (260 mg, 0.81 mmol) in 20 mL of THF/20 mL of piperidine. After the mixture had been stirred under argon for 19 h, the solvent was evaporated and the residue was dissolved in 100 mL of CH_2Cl_2. The solution was extracted with 50 mL of NH_4Cl, 50 mL of water, and 50 mL of $NaHCO_3$. The organic layer was dried over Na_2SO_4, concentrated, and subjected to column chromatography [30 × 3 cm SiO_2, CH_2Cl_2/cyclohexane (50:1)]. Yellow crystals (120 mg, 30%) that melted at 190 °C were obtained. FT-IR (KBr): $\tilde{\nu}$ = 2961, 2928, 2875, 1515, 1464, 1429, 1387, 1275, 1211 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.07 (m, 42 H, CH_3), 1.87 (m, 28 H, CH_2), 3.86 (t, 4 H, OCH_2), 3.98 (m, 24 H, OCH_2), 6.81 (s, 4 H, arom. H), 7.01 (s, 12 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.4, 10.5 (CH_3), 22.6, 22.7, 22.8 (CH_2), 70.3, 71.3, 71.5 (OCH_2), 89.9, 91.4, 91.6 (acetyl. C), 114.2, 114.3, 114.5, 114.6, 114.9, 116.7, 117.7, 117.8, 118.8 (arom. C), 153.0, 153.6, 154.1 (C_qO) ppm.[34] MS (FD): *m/z* (%) = 1494 (96), 747 (100), 498 (3); the peaks correspond to $[M + 2 H]^+$, $[M + 2 H]^{2+}$ and $[M + 2 H]^{3+}$. $C_{96}H_{114}O_{14}$(1492.0): calcd. C 77.29, H 7.70; found C 77.31, H 7.76.

1-[2,5-Dipropoxy-4-(2,5-dipropoxyphenylethynyl)phenylethynyl]-4-[2,5-dipropoxy-4-(triisopropylsilylethynyl)phenylethynyl]-2,5-dipropoxybenzene (9): Triphenylphosphane (100 mg, 0.38 mmol), CuI (74 mg, 0.39 mmol), and $Pd(PPh_3)_2Cl_2$ (134 mg, 0.19 mmol) were added to a degassed solution of **7**[31] (5.0 g, 7.68 mmol) and **8**[31] (4.04 g, 8.07 mmol) in 120 mL of piperidine. The mixture was stirred under argon at 50 °C for 1 h and at 20 °C for 72 h. The solvent was removed, and the residue was treated with 150 mL of CH_2Cl_2. After extraction with 50 mL of NH_4Cl, 50 mL of water, and 50 mL of $NaHCO_3$, the solvent was evaporated and the residue was filtered through 10 × 5 cm SiO_2 with $CHCl_3$. Column chromatography (50 × 3 cm SiO_2, toluene and then toluene/cyclohexane 10:1) yielded yellow crystals (6.57 g, 84%), which melted at 112 °C. ^{1}H NMR ($CDCl_3$): δ = 1.05 (m, 45 H, CH_3, $CH(CH_3)_2$], 1.83 (m, 16 H, CH_2), 3.87 (m, 4 H, OCH_2), 3.99 (m, 12 H, OCH_2), 6.81 (m, 2 H, arom. H), 6.93−7.03 (m, 7 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.5, 10.6 (CH_3), 11.4 (CH of isopropyl), 18.7 (CH_3 of isopropyl), 22.6, 22.7, 22.8 (CH_2), 70.2, 70.9, 71.2, 71.4, 71.5 (OCH_2), 89.8, 91.4, 91.6, 96.5, 103.1 (acetyl. C), 114.0, 114.1, 114.4, 114.7, 116.6, 116.8, 117.5, 117.6, 118.0, 118.7 (arom. C), 152.9, 153.3, 153.5, 154.0, 154.4 (C_qO) ppm.[34] MS (FD): *m/z* (%) = 1024 (100) $[M + H]^+$, 512 (31) $[M + H]^{2+}$. $C_{65}H_{86}O_8Si$ (1023.5): calcd. C 76.28, H 8.47; found C 76.13, H 8.61.

1-[2,5-Dipropoxy-4-(2,5-dipropoxyphenylethynyl)phenylethynyl]-4-(2,5-dipropoxy-4-ethynylphenyl)-2,5-dipropoxybenzene (10): Compound **9** (6.25 g, 6.11 mmol) in 70 mL of THF was treated with $(C_4H_9)_4N^+F^-$ (2.89 g, 9.16 mmol). The yellow solution immediately turned red-brown. After 5 min stirring, the solvent was removed, and the residue was dissolved in 100 mL of chloroform and extracted with 100 mL of water. The organic layer was dried over Na_2SO_4 and concentrated. Column chromatography (80 × 2 cm SiO_2, toluene) yielded yellow crystals (3.51 g, 66%), which melted at 126 °C. ^{1}H NMR ($CDCl_3$): δ = 1.07 (m, 24 H, CH_3), 1.84 (m, 16 H, CH_2), 3.33 (s, 1 H, acetyl. H), 3.83 (t, 2 H, OCH_2), 3.98 (m, 14 H, OCH_2), 6.81 (m, 2 H, arom. H), 6.96−7.03 (m, 7 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.4, 10.5, 10.6 (CH_3), 22.6, 22.7, 22.8 (CH_2), 70.2, 71.1, 71.2, 71.3, 71.4 (OCH_2), 80.1, 82.3, 89.8, 91.2, 91.4, 91.6, 91.7 (acetyl. C), 112.6, 114.1, 114.2, 114.4, 114.6, 114.7, 115.1, 116.7, 117.2, 117.5, 118.1, 118.6 (arom. C), 152.9, 153.3, 153.4, 154.0, 154.1 (C_qO) ppm.[34] MS (FD): *m/z* (%) = 867 (100) $[M + H]^+$, 434 (8) $[M + H]^{2+}$. $C_{56}H_{66}O_8$ (867.1): calcd. C 77.57, H 7.67; found C 77.18, H 7.97.

1-(4-Bromo-2,5-dipropoxyphenylethynyl)-4-[2,5-dipropoxy-4-(2,5-dipropoxyphenylethynyl)phenylethynyl]-2,5-dipropoxybenzene (12): Triphenylphosphane (20.1 mg, 0.077 mmol), CuI (14.6 mg, 0.077 mmol), and $Pd(PPh_3)Cl_2$ (27.0 mg, 0.039 mmol) were added to a degassed solution of **7**[31] (1.0 g, 1.54 mmol) and **11**[31] (0.75 g, 1.85 mmol) in 120 mL of piperidine. After the mixture had been stirred under nitrogen at 50 °C for 4 h and at 20 °C for 12 h, the solvent was removed and the residue was treated with 200 mL of CH_2Cl_2. The solution was extracted with 100 mL of NH_4Cl, 100 mL of water, and 100 mL of $NaHCO_3$ and dried over Na_2SO_4, and the solvents were evaporated. Twofold column chromatography (15 × 4 cm SiO_2/toluene and then 30 × 2 cm SiO_2/toluene/cyclohexane (5:1) yielded yellow crystals (540 mg, 38%), which melted at 130 °C. ^{1}H NMR ($CDCl_3$): δ = 1.06 (m, 24 H, CH_3), 1.82 (m, 16 H, CH_2), 3.86 (t, 2 H, OCH_2), 3.98 (m, 14 H, OCH_2), 6.81 (m, 2 H, arom. H), 7.00−7.08 (m, 7 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.6 (CH_3), 22.6, 22.7, 22.8 (CH_2), 70.2, 71.1, 71.2, 71.4, 71.5, 71.6 (OCH_2), 89.8, 90.6, 90.8, 91.4, 91.6 (acetyl. C),

113.1, 113.3, 114.0, 114.1, 114.2, 114.4, 114.5, 114.7, 116.6, 117.4, 117.5, 117.9, 118.3, 118.6 (arom. C), 149.5, 152.9, 153.5, 154.0 (C_qO) ppm.[34] MS (FD): *m/z* (%) = 921/923 (100) $[M + H]^+$, Br isotope pattern, 462/461 (7) $[M + H]^{2+}\cdot$ $C_{54}H_{65}BrO_8$ (922.0): calcd. C 70.35, H 7.11; found C 70.48, H 7.08.

Heptamer OPE 1g: The catalyst, consisting of triphenylphosphane (3.0 mg, 0.011 mmol), CuI (2.2 mg, 0.012 mmol), and $Pd(PPh_3)_3Cl_2$ (4.0 mg, 0.006 mmol), was added to a degassed solution of **10** (200 mg, 0.228 mmol) and **12** (260 mg, 0.282 mmol) in 70 mL of piperidine. After the mixture had been stirred under argon at 50 °C for 1 h and at 20 °C for 28 h, the solvent was removed, and the residue was dissolved in 50 mL of chloroform and extracted with 25 mL of NH_4Cl, 25 mL of water, and 25 mL of $NaHCO_3$. The organic phase was dried over Na_2SO_4, filtered through SiO_2 (10 × 5 cm) with chloroform, and purified by column chromatography (50 × 2 cm SiO_2) with a solvent gradient changing from CH_2Cl_2/toluene 5:1 via CH_2Cl_2/cyclohexane 5:1 to toluene/cyclohexane 1:1. Yellow crystals (20 mg, 5%) were isolated, and these melted at 204 °C. FT-IR (KBr): $\tilde{\nu}$ = 2963, 2934, 2876, 1515, 1428, 1387, 1275, 1211 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.07 (m, 48 H, CH_3), 1.84 (m, 32 H, CH_2), 3.86 (t, 4 H, OCH_2), 3.99 (m, 28 H, OCH_2), 6.81 (s, 4 H, arom. H), 7.01 (s, 14 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.6 (CH_3), 22.7 (CH_2), 70.3, 71.2, 71.4 (OCH_2), 89.8, 91.4, 91.6 (acetyl. C), 114.0, 114.1, 114.4, 114.7, 117.4, 117.5, 118.7 (arom. C), 152.9, 153.5, 154.0 (arom. C_qO) ppm. MS (FD): *m/z* (%) = 1710 (36), 855 (100), 570 (16), 428 (1); the peaks correspond to $[M + 2H]^+$, $[M + 2H]^{2+}$, $[M + 2H]^{3+}$ and $[M + 2H]^{4+}$. $C_{110}H_{130}O_{16}$ (1708.2): calcd. C 77.34, H 7.67; found C 77.04, H 7.63.

Octamer OPE 1h: Triphenylphosphane (16 mg, 0.064 mmol), CuI (12 mg, 0.064 mmol), and $Pd(PPh_3)_2Cl_2$ (22 mg, 0.033 mmol) were added to a degassed solution of **13**[31] (1.0 g, 1.28 mmol) and **7**[31] (1.9 g, 2.92 mmol) in 20 mL of toluene/8 mL of piperidine. The mixture was stirred under argon at 50 °C for 18 h, the solvent was removed, and the residue was treated with 50 mL of CH_2Cl_2. The solution was extracted with 50 mL of NH_4Cl, 50 mL of water, and 50 mL of $NaHCO_3$. The dried (Na_2SO_4) and concentrated organic phase was subjected to column chromatography (20 × 2 cm SiO_2; CH_2Cl_2/toluene, 5:1 with a gradient to 10:1). The raw product was dissolved in 3 mL of CH_2Cl_2, to which 50 mL of cyclohexane were then added, so that the pure compound **1h** started to crystallize. Yellow crystals (80 mg, 3%) were obtained, and these melted at 202 °C. FT−IR (KBr): $\tilde{\nu}$ = 2964, 2936, 2876, 1512, 1473, 1427, 1388, 1274, 1211 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.05 (m, 54 H, CH_3), 1.85 (m, 36 H, CH_2), 3.86 (t, 4 H, OCH_2), 4.00 (m, 32 H, OCH_2), 6.81 (s, 4 H, arom. H), 7.02 (s, 12 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.4, 10.5 (CH_3), 22.6, 22.7, 22.8 (CH_2), 70.3, 71.3, 71.5 (OCH_2), 89.8, 91.4, 91.6 (acetyl. C), 114.2, 114.3, 114.5, 114.6, 114.9, 117.6, 117.7, 118.8 (arom. C), 152.9, 153.5, 154.0 (arom. C_qO) ppm.[34] MS (FD): *m/z* (%) = 1926 (76), 963 (100), 642 (33), 482 (3); the peaks correspond to $[M + 2H]^+$, $[M + 2H]^{2+}$, $[M + 2H]^{3+}$ and $[M + 2H]^{4+}$. $C_{124}H_{130}O_{16}$ (1924.5): calcd. C 77.39, H 7.65; found C 77.28, H 7.60.

Decamer OPE 1i: $Pd(PPh_3)_2Cl_2$ (2.8 mg, 0.0054 mmol), CuI (2.0 mg, 0.0105 mmol), and triphenylphosphane (2.4 mg, 0.0107 mmol) were added to a degassed solution of **14**[31] (260 mg, 0.240 mmol) and **15**[31] (48 mg, 0.108 mmol) in 50 mL of piperidine. The yellow solution was stirred under argon at 50 °C for 3 h and then at 20 °C for 48 h. The solvent was removed and the residue was dissolved in chloroform. After extraction with 20 mL of NH_4Cl, 20 mL of water, and 20 mL of $NaHCO_3$, the organic phase was dried over Na_2SO_4 and concentrated. Column chromatography on SiO_2 (20 × 3 cm) with $CHCl_3$ was followed by further column chromatography (30 × 3 cm SiO_2) with a toluene/CH_2Cl_2 gradient from 1:1 to 1:3. Yellow crystals (48 mg, 22%) were obtained, and these did not melt below 220 °C, but started to decompose at this temperature. FT−IR (KBr): $\tilde{\nu}$ = 2964, 2934, 2876, 1512, 1427, 1388, 1275, 1212 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.07 (m, 66 H, CH_3), 1.84 (m, 44 H, CH_2), 3.87 (t, 4 H, OCH_2), 4.00 (m, 40 H, OCH_2), 6.81 (s, 4 H, arom. H), 7.01 (s, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.6 (CH_3), 22.7, 22.8 (CH_2), 70.3, 71.2, 71.4 (OCH_2), 89.8, 91.4, 91.6 (acetyl. C), 114.0, 114.4, 114.7, 117.5, 118.7 (arom. C), 152.9, 153.5, 154.0 (arom. C_qO) ppm.[34] MS (FD): *m/z* (%) = 2359 (100), 1180 (69), 787 (26), 590 (4); the peaks correspond to $[M + 3H]^+$, $[M + 3H]^{2+}$, $[M + 3H]^{3+}$ and $[M + 3H]^{4+}$. $C_{152}H_{178}O_{22}$ (2357.1): calcd. C 77.46, H 7.61; found C 76.86, H 8.00.

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