Pentadecamer 2,5-Dipropoxy-1,4-phenylenevinylene

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The conjugated, all-(*E*)-configured pentadecamer 2,5-dipropoxy-1,4-phenylenevinylene **1j** was prepared by a multistep synthesis on the basis of hydroquinone. The procedure consists of a general method for the repetitive extension of oligo(phenylenvinylene) chains by two styryl units (**7a** → **10** → **12** → **14**). The relatively rigid oligomer **1j** represents a molecular wire of about 100 Å. The absorption of **1j** provides a proof for the convergence theory for electronic properties of conjugated oligomers with increasing number of repeat units. The corresponding conjugated polymer **1p** with the same substitution matches the values which were extrapolated from the oligomer series **1a**–**1j**.
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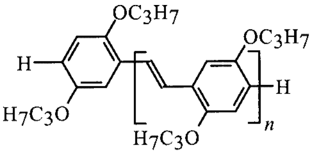
Introduction

Oligo- and poly(phenylenevinylene)s (OPVs and PPVs) represent a highly interesting class of compounds in materials science. Various applications in light emitting diodes (LEDs), in semiconductive or photoconductive devices, in nonlinear optics, conversion of sunlight, etc. have been reported.[1]

We showed in early studies [2,3] that the 2,5-substitution of the benzene rings with propoxy groups guarantees an optimum photoconductivity. Shorter or much longer alkoxy side chains are less favorable concerning the solubility and processability and/or the charge transfer from chain to chain.

Another important feature concerns the length of the main chain. The formation of charge carriers and their transport depend on the HOMO−LUMO gap (band gap in the solid state). Therefore the effective conjugation length (ECL) plays an important role.[1j] Some time ago, we found that the usual hyperbolic approximation by plotting the energy E_n of the electronic transition versus $1/n$ leads to a wrong prediction for the limiting value E_∞ ($n \rightarrow \infty$).[4,5] The reason for this failure is due to the saturation phenomenon which causes a bent of the "linear" plot E_n versus $1/n$. This bent appears for $n > 8$ in the oligomer series **1**. Therefore, we suggested an algorithm based on exponential functions (natural growth functions) for the data fit and the extrapolation of the energies of the absorption and the fluorescence of conjugated oligomers.[4]

It turned out that the OPV series **1** (Scheme 1) measured in $CHCl_3$ has an ECL of $n = 11$ and a limiting value $E_\infty = 2.59$ eV which corresponds to $\lambda_\infty = 481$ nm. Among the 9 oligomers prepared in this series, the highest oligomer was the undecamer ($n = 11$) which just reached the convergence limit with λ_{max} (11) = 481 nm. In order to establish the extrapolation method, we extended now our study to the pentadecamer ($n = 15$), whose absorption should be located right on the convergence plateau.



1	a	b	c	d	e	f	g	h	i	j
n	1	2	3	4	5	6	7	8	11	15

Scheme 1. Oligo(2,5-dipropoxy-1,4-phenylenevinylene)s **1a**−**1j**

Results and Discussion

The synthesis of monodisperse, i.e. constitutionally and configurationally pure oligomers with high *n* values demands special, at its best convergent strategies. The reduced solubility of long conjugated chains as well as their reduced capability to enter reactions on the very end of the chain led us to a strategy in which the pentadecamer **1a** should be generated by the formation of a C−C double bond between two identical (functionalized) heptamers. The McMurry reaction seemed to be a suitable process for the last step.

Scheme 2 summarizes the whole synthetic sequence. The hydroquinone derivatives **2a**,**b** were transformed by a photobromination to the dibromo compound **3** and by a

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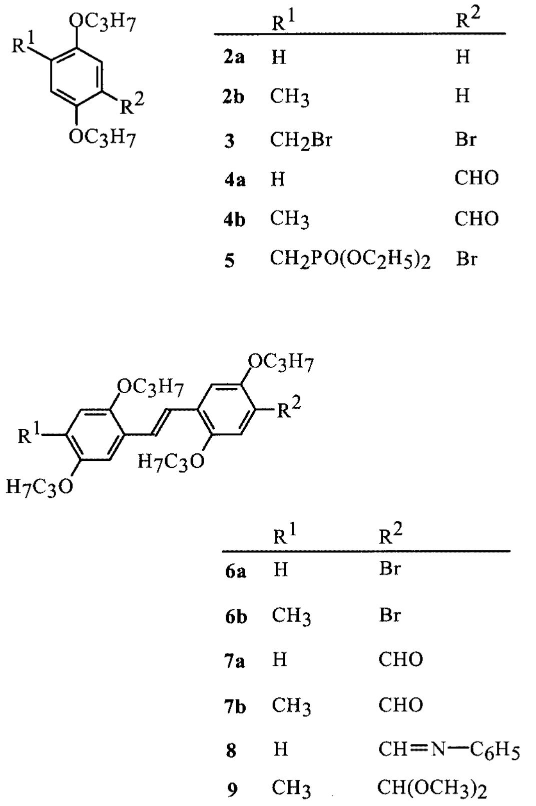
Rieche−Gross[6,7] formylation to the aldehydes **4a**,**b**.[3,8] The phosphonate **5**, obtained in a Michaelis−Arbuzov reaction of **3**, yielded in a Wittig−Horner reaction with **4a**,**b** the stilbenes **6a**,**b**.[3,8] Displacement of the bromo substituent by a formyl group in a Bouveault process[9] furnished the aldehydes **7a**,**b**.[3] Subsequently, **7a** was transformed into the *N*-phenylimine **8** and **7b** to the acetal **9**.



	R^1	R^2
2a	H	H
2b	CH_3	H
3	CH_2Br	Br
4a	H	CHO
4b	CH_3	CHO
5	$CH_2PO(OC_2H_5)_2$	Br

	R^1	R^2
6a	H	Br
6b	CH_3	Br
7a	H	CHO
7b	CH_3	CHO
8	H	$CH{=}N{-}C_6H_5$
9	CH_3	$CH(OCH_3)_2$

Scheme 2. Preparation of functionalized stilbenes

The protection of the aldehyde function was necessary for the selective Siegrist condensation[10,11] **8** + **9** → **10**. Thus, the conjugation in aldehyde **7a** was extended by two styryl units which led to the aldehyde **10**. Repetition of the two latter steps gave via *N*-phenylimine **11** the aldehyde **12** and from there via *N*-phenylimine **13** the aldehyde **14** (Scheme 3).

Acidic workup led directly to a deprotection of the formyl group so that the generated aldehyde could be used for the next "homologisation". This procedure turned out to be very convenient and efficient in order to extend the conjugated chain of an OPV or a related system stepwise by adding a *trans*-stilbene unit. Normally, benzaldehydes can be transformed to stilbenes in good yields by applying the McMurry reaction; however, in the case of **14** the reaction led to a mixture of products. In order to avoid a difficult separation procedure we stopped the process at an early stage and isolated pure **1j** in a moderate yield.

All C−C double bonds in **6**−**14** and particularly in **1j** have (*E*) configuration. The Siegrist reaction is a kinetically controlled process with an extremely high *trans* selectivity;[12] however, the Wittig−Horner reaction as well as the McMurry reaction are not as stereoselective. The solubility of the overall (*E*)-configured compounds is always lower than the solubility of the diastereomers with one or more (*Z*) configurations; therefore crystallisation is the method of choice for the final purification. The detection limit for a *cis*-stilbene moiety by ^1H NMR spectroscopy lies between 3 and 5%. There is no indication for a (*Z*) configuration − neither in the target compound **1j** nor in its precursor **14**.

The solubility of the all-(*E*)-configured pentadecamer OPV **1j** in $CDCl_3$ or other NMR solvents is relatively low so that we preferred solid-state CPMAS NMR spectroscopy.

The ^{13}C NMR signals at $\delta = 11$, 22, and 72 ppm can be attributed to the propoxy side chains. The peak at $\delta = 108$ ppm corresponds to the methine groups in α-position to the oxygen atom bearing quaternary carbon atoms which show a sharp resonance at $\delta = 150$ ppm. The remaining olefinic CH groups and quaternary aromatic carbon atoms lead to signals at $\delta \approx 120$ and 127 ppm.

The mass spectrum of **1j**, recorded with the MALDI-TOF technique contains the peak group of the molecular ions with a maximum at $m/z = 3468.3$; the calculated value is 3468.1. Although the $M^{+\cdot}$ ions cannot be detected in the FD-MS spectrum, the latter shows the $[M^{2+}]$, $[M^{3+\cdot}]$, $[M^{4+}]$ and $[M^{5+\cdot}]$ ions of **1j**.

The UV/Vis spectrum of **1j** in $CHCl_3$ exhibits a long-wavelength absorption with a maximum at $\lambda = 482$ nm. An exact determination of the absorption intensity is difficult because of the low solubility; nevertheless, the obtained ε value of about 2.6×10^5 $cm^2{\cdot}mmol$ fits into the general approximation which was found for series **1** [Equation (1)].[4,8]

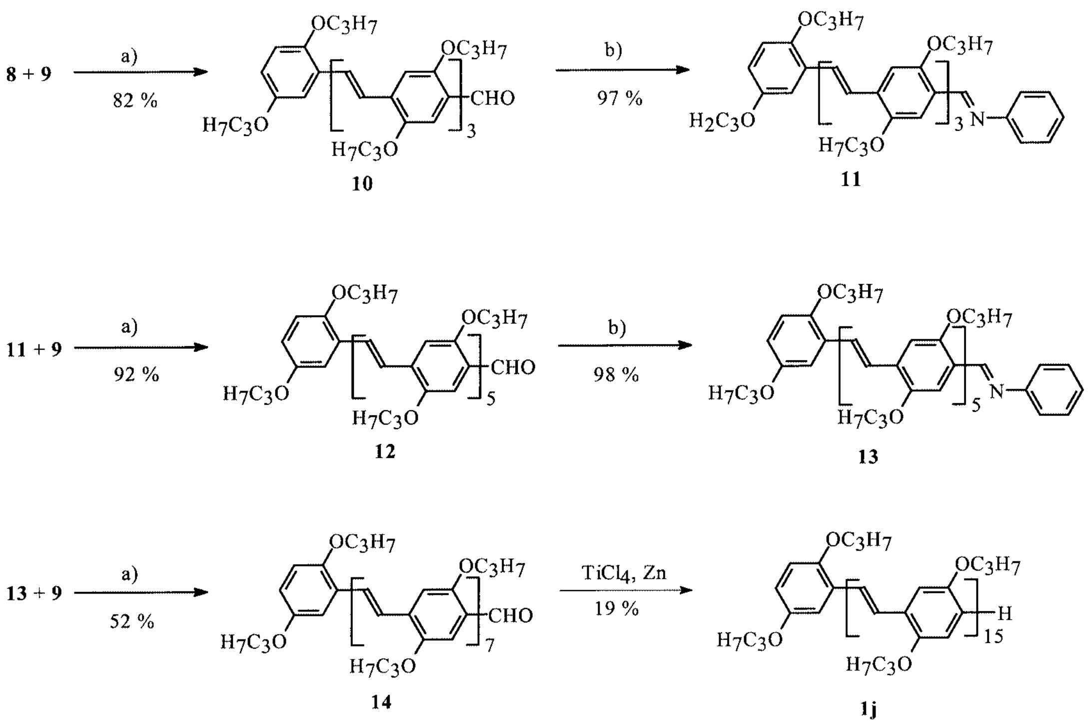
$$\log \varepsilon \approx \log n + 4.28 \tag{1}$$

On the basis of this equation, one would predict for $n = 15$ an ε value of about 2.8×10^5 $cm^2{\cdot}mmol$. Figure 1 exhibits a plot of the absorption maxima λ_{max} and the absorption edges $\lambda_{0.1}$ [13] versus the number *n* of repeat units. It clearly shows that the absorption of **1j** is in the range of the limiting value λ_∞ for the oligomer series **1**. The fit function [Equation (2)][4] and the term for the effective conjugation length [Equation (3)] led to the data listed in Table 1. The absorption bands of seven selected members of the series **1** were depicted in context with the preparation of these oligomers.[8]

$$\lambda_{in} = \lambda_{i\infty} - (\lambda_{i\infty} - \lambda_{i1})e^{-b(n-1)} \tag{2}$$

$$n_{ECL} = 1 + [\ln(\lambda_\infty - \lambda_1)]/b \tag{3}$$

Now the crucial question is, how does the measurement of poly(2,5-dipropoxyphenylenevinylene)s **1p** agree with the predicted λ_∞ values. Defects in the chain, like saturated car-



Scheme 3. Synthesis of the pentadecamer OPV **1j**: a) $KOC(CH_3)_3$, DMF; b) $C_6H_5{-}NH_2$

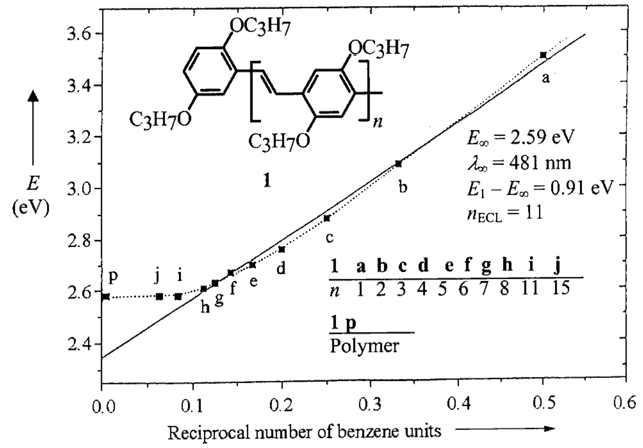


Figure 1. Energies E of the absorption maxima of **1a**−**1j** in chloroform and their exponential fit function (dotted line), which approaches the transition energy of the polymer **1p**

Table 1. Convergence data of the absorption of the OPV series **1**

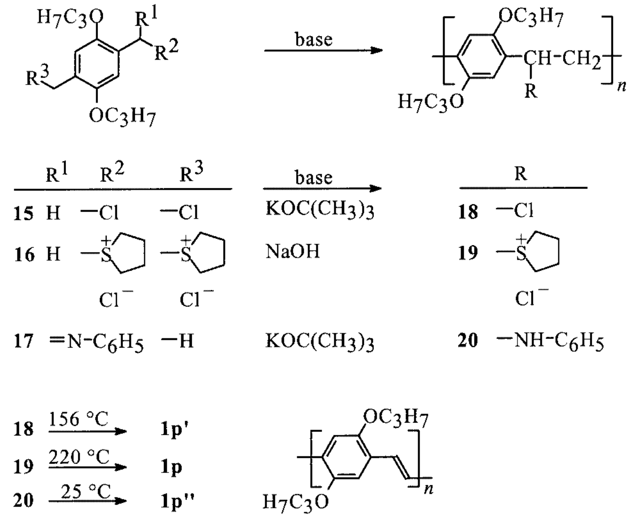
	Absorption maxima[a]	Absorption edges[a]
λ_1	354 nm	394 nm
λ_{11}	481 nm	543 nm
λ_{15}	482 nm	543 nm
λ_∞	481 nm	543 nm
b	0.4571 ± 0.0092	0.4837 ± 0.0063
n_{ECL}	11	11

[a] Accuracy of the spectrometer: ± 1 nm.

bon atoms or (*Z*)-configured olefinic double bonds block or impair the conjugation. We studied first the anionic polymerisation of the dichloro compound **15** with $KOC(CH_3)_3$/THF (Scheme 4). According to the method of Swatos and Gordon[14] a polymer **1p′** was obtained via the precursor polymer **18** having chloroethylene units between the benzene rings. The final extrusion of HCl in boiling cyclohexanone led to a red polymer **1p′**. Its δ values obtained in the solid-state NMR spectrum are similar to the δ values of **1j**; however, the long-wavelength absorption has in $CHCl_3$ a λ_{max} value of 477 nm and a $\lambda_{0.1}$ value of 543 nm. The small hypsochromic shift of the maximum compared to λ_∞ = 481 nm reveals that the chain contains an appreciable amount of segments with a conjugation length shorter than n_{ECL} = 11.

The polymer generation on the basis of the disulfonium salt **16** with the Wessling−Zimmerman route[15,16] yielded the precursor polymer **19** and then by heating polymer **1p** with λ_{max} = 482 nm and $\lambda_{0.1}$ = 545 nm (measurement in $CHCl_3$). Thus, the Wessling−Zimmerman procedure is superior and confirms the extrapolation.

In 1991 we found, that the alkaline condensation reaction of *N*-phenylimine of alkoxy-substituted 4-methylbenzaldehydes is a very convenient method for the preparation of soluble PPVs.[17] Applied to the 2,5-dipropoxy system, a polymer **1p″** was obtained via the non-isolable prepolymer **20**. The number of repeat units n amounted to 29−30 (NMR endgroup determination).[3] The long-wavelength absorption has a λ_{max} value of 485 nm and a $\lambda_{0.1}$ value of 545 nm. Both values exceed slightly the extrapolation ($n \to \infty$). However, one has to realize that the endgroups *N*-



Scheme 4. Routes for the generation of the polymers **1p**, **1p′** and **1p′′**

phenylimino (or formyl after hydrolysis) induce a push-pull character in the conjugated chain. The conjugation effect is superimposed by an intramolecular charge transfer effect.[18] Therefore, a bathochromic shift should be observed, when such systems are compared to chains which do not contain electron-accepting endgroups.

A newer, highly defect-free preparation of PPVs makes use of the Wittig−Horner reaction.[19] The 5-(2-ethylhexyloxy)-2-methoxy system, which is related to **1p**, exhibits in dioxane a λ_{max} value of 498 nm.[19] The exact endgroups are not known, but again one has to assume terminal electron-withdrawing substituents, namely phosphonate and/or formyl groups, which induce a charge transfer effect.

Summary and Conclusion

A synthetic sequence of 18 steps based on hydroquinone and 2-methylhydroquinone led to the pentadecamer 2,5-dipropoxy-1,4-phenylenevinylene system **1j**. The all-(*E*)-configured, monodisperse compound represents a fully conjugated rod-like molecule. The inherent conformational freedom[20] leads to a calculated length[21] of the chromophore of 99−102 Å. The UV/Vis absorption band of **1j** measured in $CHCl_3$ has a maximum at $\lambda_{max} = 482$ nm and an edge at $\lambda_{0.1} = 543$ nm. The effective conjugation length in this series **1** was determined to be $n_{ECL} = 11$. Thus, compound **1j** has an absorption which matches the limiting values $\lambda_\infty = 481$ nm for the maximum and $\lambda_{0.1} = 543$ nm for the long-wavelength edge, respectively. Since **1j** is the first studied monodisperse OPV system with $n > n_{ECL}$, it provides a proof for the convergence theory of the electronic properties of such a series of conjugated oligomers.

Moreover, the absorption bands of the PPVs **1p** exhibit the λ_{max} and $\lambda_{0.1}$ values which have been extrapolated from the OPV series **1a**−**1j**. The Wessling−Zimmerman route led to less structural defects than the anionic polymerisation.[22] As soon as electron-withdrawing endgroups are present in **1p′′**, a slight bathochromic shift of the absorption maximum is observed which can be explained by a superimposed charge transfer in the electronic transition $S_0 \rightarrow S_1$.

The effective conjugation length n_{ECL} represents a number of repeat units which is characteristic for the oligomer series as well as for the investigated property. Whereas only the ground state S_0 and the first excited singlet state S_1 are responsible for the absorption and the fluorescence spectra, more essential states determine the nonlinear optical properties. The hyperpolarizability of second order γ for example has an unknown effective conjugation length in the oligomer series **1** − in every case it is much higher than 11.[23]

Experimental Section

General Remarks: UV/Vis: Perkin−Elmer Lambda 20, $CHCl_3$ as solvent. ^1H and ^{13}C NMR: Bruker AM 400, Avance 400, $CDCl_3$/TMS as internal standard or solid state. MS: Varian MAT 70A (EI, 70 eV) or Finnigan MAT 95 (FD, accelerating voltage 5 kV). Elemental analyses: Microanalytical Laboratory of the Institute of Organic Chemistry, University of Mainz.

Syntheses: Compounds **2a**,[8] **2b**,[3] **4a**,[8] **4b**,[3] **5**,[8] **6a**,[8] **6b**,[8] **7a**,[8] **7b**,[8] **8**,[8] and **9**[8] were prepared according to the literature.

1-Bromo-4-(bromomethyl)-2,5-dipropoxybenzene (3): 26.4 g (92 mmol) of **2b** was refluxed in 150 mL of CCl_4 and irradiated with a tungsten lamp (500 W); 16.0 g (100 mmol) Br_2 was added within 45 min. The solution was washed with 50 mL of water, 50 mL of saturated $NaHCO_3$ and again 50 mL of water. The organic layer was filtered and the solvent evaporated. The oily residue was purified by distillation. Yield: 30.9 g (92%), colorless oil, b.p. 230 °C (2.24 kPa). ^1H NMR ($CDCl_3$): $\delta = 1.06$ (t, 6 H, CH_3), 1.81 (m, 4 H, CH_2), 3.92 (t, 2 H, OCH_2), 3.93 (t, 2 H, OCH_2), 4.50 (s, 2 H, CH_2Br), 6.89 (s, 1 H, 3-H), 7.05 (s, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 10.5$, 10.6 (CH_3), 22.5, 22.6 (CH_2), 28.4 (CH_2Br), 70.7, 71.7 (OCH_2), 113.2 (C-1), 116.0, 117.4 (C-3, C-6), 126.1 (C-4), 149.4, 151.2 (C-2, C-5) ppm. EI-MS (70 eV): *m/z* (%) = 368, 366, 364 (10) [$M^{+\cdot}$], Br_2 pattern, 287, 285 (32), Br pattern, 42 (100). $C_{13}H_{18}Br_2O_2$ (366.1): calcd. C 42.65, H 4.96, Br 43.65; found C 42.75, H 4.90, Br. 43.45.

General Procedure for the Extension of an OPV Aldehyde by Two Styryl Units: Solutions of 3.6 g (32 mmol) of $KOC(CH_3)_3$ in 100 mL of dry DMF, 1.6 mmol of aldimine in 100 mL of dry DMF and 0.80 g (1.6 mmol) of acetal **9** in 50 mL of dry DMF were prepared and degassed. The solution/suspension of the aldimine was added within 5 min to the base before the solution of **9** was added dropwise within 20 min into the reaction vessel. All these procedures were performed under argon. TLC control (SiO_2; DMF) revealed the complete consumption of **9** within 4−6 h. (Raising the temperature from 25 to 80 °C reduced the reaction time to less than 1 h, but led to some side products.) The mixture was poured on crushed ice, treated with 50 mL of HCl (6 M) and extracted 3 times with 50 mL of CH_2Cl_2 each. The combined organic phases were washed with water and $NaHCO_3$, dried with Na_2SO_4, filtered and the solvents evaporated. Purification and spectroscopic characterization of **10**, **11** and **12** were performed as described.[8]

all-(*E*)-*N*-Phenyl-2,5-dipropoxy-4-[2,5-dipropoxy-4-(2,5-dipropoxy-4-{2,5-dipropoxy-4-[2,5-dipropoxy-4-(2,5-dipropoxystyryl)-styryl]styryl}styryl)styryl]benzaldimine (13): The aldehyde **12** (3.6 g, 2.74 mmol) was treated at 60 °C and 10 kPa with 30 mL (30.4 g, 326 mmol) of freshly distilled aniline for 1.5 h. The excess aniline was removed and the residue recrystallized from ethanol/chloroform (2:1, 1.8 L); 3.7 g (98%) orange crystals were obtained, which melted at 225 °C. ^1H NMR ($CDCl_3$): δ = 1.06 (m, 36 H, CH_3), 1.87 (m, 24 H, CH_2), 3.96 (m, 24 H, OCH_2), 6.79 (m, 2 H, aromat. H of outer benzene ring), 7.25 (m, 13 H, aromat. H), 7.42 (m, 2 H, *o*-H, *N*-phenyl), 7.60 (m, 10 H, olefin. H), 7.74 (s, 1 H, aromat. H), 8.95 (s, 1 H, CHN) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.7, 10.9, 11.0 (CH_3), 23.2, 23.3, 23.4 (CH_2), 70.7, 71.4, 71.5, 71.6 (OCH_2), 110.8, 111.1, 111.2, 111.4, 112.8, 114.5, 121.4, 129.5 (aromat. CH), 123.8, 124.0, 124.2, 124.3, 125.3, 126.0 (olefin. CH), 127.5, 127.9, 128.1, 128.5, 128.6 (aromat. C_q), 151.6, 151.7, 151.9, 153.4, 153.9, 154.4 (C_qO), 156.2 (CHN) ppm. FD MS: *m*/*z* (%) = 1389 (66) $[M^{+}\cdot]$, 695 (100) $[M^{2+}]$. $C_{89}H_{113}NO_{12}$ (1388.9): calcd. C 77.53, H 7.53, N 1.02; found C 77.47, H 7.32, N 0.99.

all-(*E*)-2,5-Dipropoxy-4-(2,5-dipropoxy-4-{2,5-dipropoxy-4-[2,5-dipropoxy-4-(2,5-dipropoxy-4-{2,5-dipropoxy-4-[2,5-dipropoxy-4-(2,5-dipropoxy-styryl)styryl]styryl}styryl)benzaldehyde (14): The above-described preparation was followed by a column chromatography (SiO_2; dichloromethane/cyclohexane, 2:1); 1.45 g (52%) of a red solid was obtained, which started to decompose above 230 °C. ^1H NMR ($CDCl_3$): δ = 1.07 (m, 48 H, CH_3), 1.87 (m, 32 H, CH_2), 3.98 (m, 32 H, OCH_2), 6.76 (m, 2 H, aromat. H), 7.16 (m, 14 H, aromat. H), 7.32 (s, 1 H, aromat. H), 7.50 (m, 14 H, olefin. H), 10.44 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.5, 10.5, 10.6, 10.7 (CH_3), 22.7, 22.8, 22.9, (CH_2), 70.3, 70.8, 70.8, 71.1, 71.3 (OCH_2), 110.4, 110.7, 110.8, 111.0, 111.2, 111.4, 112.5, 114.3, 114.5 (aromat. CH), 122.8, 123.3, 123.6, 123.7, 124.0, 124.2, 127.3 (olefin. CH), 126.6, 127.5, 127.7, 127.9, 128.5, 128.8, 135.4 (aromat. C_q), 150.8, 151.1, 151.2, 151.3, 151.6, 153.5, 156.3 (C_qO), 189.0 (CHO) ppm. FD MS: *m*/*z* (%) = 1750 (15) $[M^{+}\cdot]$, 875 (100) $[M^{2+}]$. $C_{111}H_{144}O_{17}$ (1750.4): calcd. C 76.17, H 8.29; found C 76.12, H 8.26.

all-(*E*)-2,2′,5,5′-Tetrapropoxy-4,4′-bis(2,5-dipropoxy-4-{2,5-dipropoxy-4-[2,5-dipropoxy-4-(2,5-dipropoxy-4-{2,5-dipropoxy-4-[2,5-dipropoxy-4-(2,5-dipropoxystyryl)styryl]styryl}styryl)styryl]-styryl}styryl)stilbene (1j): Nitrogen was purged through a suspension of 0.17 g (2.64 mmol) of Zn in 14 mL of THF at 0 °C, before 0.15 mL (0.25 g, 1.32 mmol) of $TiCl_4$ was added with a syringe. The mixture was heated to reflux for 30 min, cooled and treated with 0.27 mL of pyridine. A solution of 0.4 g (0.23 mmol) of **14** in 15 mL of dry THF was added through a syringe. After stirring for 1.5 h, the mixture was poured onto crushed ice and acidified with HCl (6 M). The red precipitate was filtered, washed with water, $NaHCO_3$, water and a small portion of CH_2Cl_2. Yield: 0.15 g (19%) of a red solid, which decomposed above 290 °C. ^1H NMR (solid state): δ = 1.0 (96 H, CH_3), 2.1 (64 H, CH_2), 4.0 (64 H, OCH_2), 7.1 (34 H, aromat. H), 7.4 (30 H, olefin. H) ppm. ^{13}C CPMAS NMR (solid state): δ = 11 (CH_3), 22 (CH_2), 72 (OCH_2), 108 (aromat. CH), 120 (olefin. CH), 127 (aromat. C_q), 150 (C_qO) ppm. MALDI-TOF: *m*/*z* (%) = 3468 (100) $[M^{+}\cdot]$. $C_{222}H_{288}O_{32}$ (3468.7): calcd. C 76.87, H 8.37; found C 76.34, H 8.14.

PPV: The PPVs were prepared from **15**,[14,22] **16**[15,16,22] and **17**[3,17] according to the literature. The red materials **1p′**, **1p** and **1p′′** gave in $CHCl_3$ slightly different UV/Vis spectra − as shown above − and very similar ^{13}C NMR spectra in the solid state: δ = 10.8−11.1 (CH_3), 23.4−23.8 (CH_2), 70.2−71.0 (OCH_2), 107.0−108.5 (aromat. CH), 119.0−121.5 (olefin. CH), 127.0−127.5 (aromat. C_q), 151.1−151.4 (C_qO) ppm.

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