Synthesis, Structure and Solvatochromism of the Emission of Cyano-Substituted Oligo(phenylenevinylene)s

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Strongly luminescent and highly soluble oligo(phenylenevinylene)s with five benzene rings and cyano groups in different positions of the terminal styrene units were prepared by means of Horner and Knoevenagel reactions. The substitution pattern – cyanide moieties on the vinyl or on the aromatic regions, together with the effect of auxochromic groups – has distinct influences on the electronic spectra, particularly on the fluorescence. Polar solvents induce red shifts and strongly reduce the fluorescence intensity of the vinyl-substituted oligomers. Cyano substitution increases the electron affinity of the oligomers; this effect is more pronounced for molecules with vinyl cyanides and can be altered by the presence of additional electron-donating or electron-withdrawing groups. The molecular structures of one oligomer bearing cyano groups on the vinylene segments and one with benzonitrile units have been resolved.

Introduction

Organic compounds with extended conjugated systems display unusual semiconducting and luminescence properties. Since the discovery of electroluminescence from poly(phenylenevinylene) (PPV),[1] interest in this polymer and its derivatives has increased steadily. These materials are promising candidates as emissive layers in light-emitting diodes (LEDs),[2-6] as well as for non-linear optics or photoconducting devices.[7,8]

The light emission of LEDs is generated by the recombination of electrons and holes injected from the electrodes into the luminescent layer. Balanced charge injection and charge carrier mobilities are decisive for high device efficiencies.[9] The ease of charge injection is determined by the barriers between the molecular frontier orbitals and the work functions of the electrodes. Most PPV-type polymers have smaller barriers to hole injection from ITO (indium tin oxide) than to electron injection from aluminium. To facilitate electron injection, metals with low work functions (Mg or Ca) can be used as electrodes, but a more practical approach is to increase the electron affinity of the luminescent material. Cyano-substituted PPV has been used as an electron-transporting material in a highly efficient two-layer LED with PPV as hole-transporting layer.[10] Emitting materials of this type with increased electron affinity are of great interest for improvement of the efficiencies of these devices.[11-13] In addition to conjugated polymers, copolymers with luminescent segments or side chains are also attractive materials for LEDs.[14,15] Oligo(phenylenevinylene)s (OPVs) can serve as model compounds for the corresponding polymers,[16] as emissive units in alternating copolymers and as electrooptical materials in their own right.[17]

Cyano substitution strongly alters the properties of oligo(phenylenevinylene)s; increased electron affinity is accompanied by strong bathochromic shifts of the absorption and emission spectra.[18,19] Calculations on cyano-substituted PPVs have shown an overall stabilisation and a distinct sensitivity of the polymer properties towards the relative positions of electron-withdrawing and electron-donating groups.[20] The stabilization of the conduction band is more pronounced if the nitrile is attached to the vinylene moiety than if it is ring-substituted, but on the other hand vinylene substitution greatly reduces the bandgap. Moreover, the rates of reaction between OPVs and singlet oxygen − the principal degradation pathway of these materials in LEDs − are strongly reduced by substitution with cyano groups, as has been shown with a series of distyrylbenzenes.[21] Cyano-substituted OPVs have been studied intensively,[22-24] the chromophores mostly being distyrylbenzenes with propenenitrile segments; only a few compounds with extended conjugated systems[25,26] or benzonitrile units have been reported so far. These model compounds can also be valuable materials for electrooptical devices, due to their luminescent and semiconducting properties, and as luminescent segments in copolymers.[27,28]

Here we present our work on cyano-substituted oligo(phenylenevinylene)s **1−13**. The synthesis of a series of OPVs with a variety of different cyano substitution patterns is reported, and the electronic spectral influences of the positions of the nitriles and their interaction with other auxochromic groups are discussed. To allow comparison, the chromophore − an oligomer with five aromatic units − remains unchanged; two alkoxy side chains on the central ring guarantee good solubility in common solvents. The dependence of the fluorescence characteristics on substitution pattern and solvent polarity are investigated and the X-ray structures of two oligomers with different cyano substitution patterns are reported.

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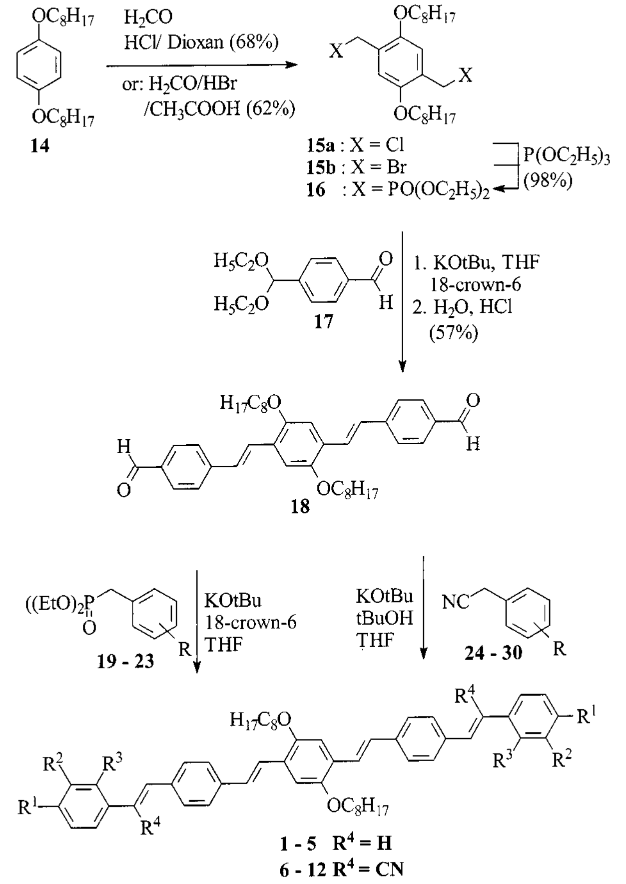
Synthesis

Wittig–Horner olefinations are among the most important tools for the synthesis of stilbene compounds. The starting materials are often easily available and these reactions tolerate an enormous diversity of functional groups. Thanks to the C_{2h} symmetry of the OPVs **1–13**, a synthetic strategy with two double olefination steps was advantageous. The central building block for these compounds was distyrylbenzene **18**, with two carbaldehyde functions in the terminal positions (Scheme 1, Table 1). Hydroquinone was first alkylated with 1-bromooctane and then treated with formaldehyde and hydrogen bromide in acetic acid, better yields could be achieved by chloromethylation in dioxane. The bis(halomethyl) compounds **15a** and **15b** were converted into the bis(phosphonate) **16** in a Michaelis–Arbuzov reaction. Double Wittig–Horner olefination with the monoprotected terephthaldialdehyde **17** and subsequent hydrolysis of the acetals directly afforded the highly fluorescent dialdehyde **18**. A THF and KO*t*Bu/18-crown-6 solvent/base system proved superior to DMF/KO*t*Bu in terms of yield and workup procedure.

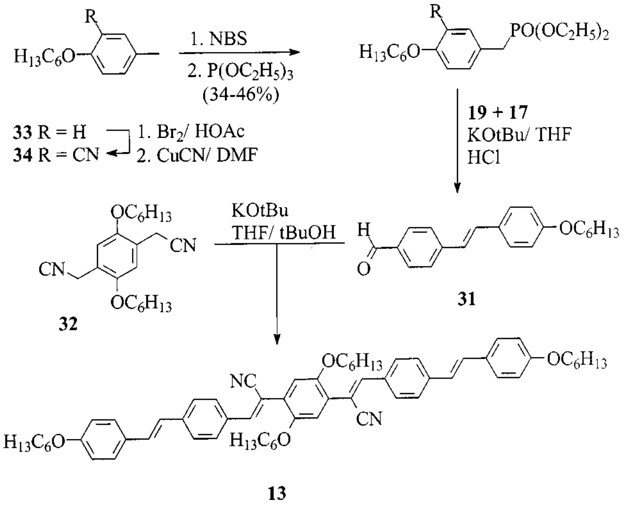


Scheme 1. Synthesis of cyano-substituted oligomers

Table 1. Substitution pattern of OPVs **1–12**

OPV	R^1	R^2	R^3	R^4	Yield (%)
1	OC_6H_{13}	H	H	H	81
2	CN				83
3		CN			77
4			CN		72
5	OC_6H_{13}	CN			74
6				CN	64
7		CF_3		CN	79
8		OCH_3		CN	72
9			OCH_3	CN	57
10	Cl			CN	97
11	CF_3			CN	96
12	OCH_3			CN	84

The elaboration of the conjugated system of **18** to the OPVs **1–12** was performed in two ways: PO-activated olefinations with substituted benzyl phosphonates **19–23** and Knoevenagel condensations with different benzyl cyanides **24–30**. The phosphonates, with the exceptions of **19** and **22**, were prepared from commercially available benzyl bromides and chlorides (Scheme 2). 4-Hexyloxytoluene (**33**) was brominated with bromine in acetic acid and halogen/cyano exchange was performed with CuCN in DMF to give **34**. Benzylic bromination of **33** and **34** with NBS and subsequent Michaelis–Arbuzov treatment of the crude bromomethyl compounds gave the phosphonates **19** and **22**.



Scheme 2. Synthesis of phosphonates **19** and **22** and OPV **13**

OPV **13** was prepared in a similar way, using Knoevenagel condensation between the bis(cyanomethyl)benzene **32** and hexyloxystilbenecarbaldehyde **31**, prepared from **17** and **19** as in Scheme 1. The cyano-substituted oligomers form luminescent crystals with colours ranging from yellow to dark red and are highly soluble in common solvents such as dichloromethane or toluene. The yellow solutions of the OPVs display very strong fluorescence as their outstanding feature.

Optical and Electronic Properties

The electronic spectra were measured under ambient conditions, solvents for spectroscopy being used as received, chloroform being filtered through basic alumina prior to use. The concentrations were about 10^{-5} mol/L for absorption and 10^{-8} mol/L for emission spectroscopy.

The two types of OPVs (ring substitution: **1−5**; vinylene substitution: **6−12**) display very similar UV/Vis spectra, with two small maxima at 305 and 360 nm and an intense maximum at either 422 to 433 nm, for the first group, or at 441−452 nm for the latter. Relative to its isomers **8** and **12**, the absorption of **9** (433 nm) is exceptionally blue-shifted (Figure 1). Similar hypsochromic absorption shifts have been observed in oligomers with comparable local arrangements of cyano and alkoxy groups and have been accounted for in terms of increased steric interaction and reduced planarity of the π-system.[25] In the absorption spectra of the cyano-substituted oligomers, only small changes were observed when the solvent polarity was varied over a broad range [cyclohexane ($\varepsilon = 2.06$) − dichloromethane ($\varepsilon = 9.00$) − acetonitrile ($\varepsilon = 38.8$)],[29] regardless of quadrupolar push-pull substitution in the OPVs **2−12**. With dichloromethane taken as a reference solvent, small hypsochromic shifts of up to 8 nm were observed when the spectra were measured in the less polar cyclohexane or in the very polar acetonitrile. The extinction coefficients remained constant within the margins of error arising from several dilution steps. The different cyano-substituted OPVs in Table 2 can be divided into three groups: ring substitution with the nitrile in the "nonconjugated" *m*-position (**3**, **5**), ring substitution with the nitrile in the "conjugated" *o*- and *p*-positions (**2**, **4**) and the compounds with vinylene cyanides (**6−12**). The spectra of the first group (**3**, **5**) were nearly identical with that of the reference compound **1**, whereas the conjugated electron acceptors gave rise to bathochromic shifts (8 nm) (**2**, **4**). Vinylene substitution induced a stronger red shift (up to 30 nm).

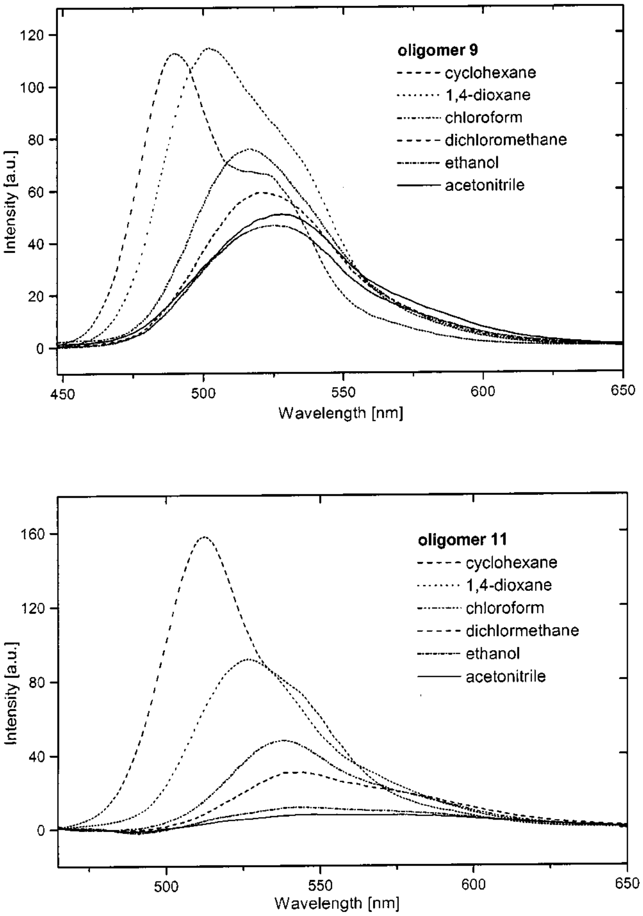


Figure 1. Fluorescence solvatochromism of **9** and **11**

All OPVs appear to be strongly fluorescent, with fluorescence quantum yields being measured in cyclohexane solution, using quinine sulfate as a standard. The photoluminescence efficiencies are in the range of 27 to 65%. In general, the fluorescence of compounds with propenenitrile segments (except for **8**) is less efficient than that of ring-substituted OPVs, while additional electron-withdrawing or electron-donating groups seem to favour radiationless decay of the excited states − although here, again, **8** behaves differently.

In cyclohexane, the fluorescence maxima are separated from the absorption maxima by Stokes shifts of 52−59 nm (2476−2733 cm^{-1}) and possess a distinct shoulder or second maximum on the red side ($\Delta\lambda \approx 25-30$ nm). The vibrational structure is blurred in dioxane and chloroform and vanishes in ethanol or acetonitrile. A stepwise increase in the polarity or dielectric constant of the solvent differentiates the fluorophores by the extent of the shift to lower energy and by the reduction, even more pronounced, of the fluorescence intensity. The fluorescence intensity of OPV **1**, without an electron-withdrawing cyano group, remains nearly constant in all solvents used, and increasing polarity causes only small bathochromic shifts of the emission, the red shift increasing in going from cyclohexane to dioxane and to chloroform and reaching its maximum value in dichloromethane (485 cm^{-1}). In the highly polar acetonitrile, the red shift is equal to the value observed in dioxane (219 cm^{-1}), while only modest in the protic ethanol (Table 3). A similar sequence was observed for the *m*-cyano-substituted OPVs (**3**, **5**). Bathochromic shifts and reduced fluorescence intensities in polar solvents are more pronounced in **3** than in **5**, indicating that the auxochromic hexyloxy group in **5** compensates for the influence of the cyano group. Conjugated nitriles (**2**, **4**) are subject to much stronger influences on the shifts of fluorescence; the emission maxima in cyclohexane and acetonitrile are separated by more than 1000 cm^{-1}, while the fluorescence intensities are reduced to 2/3 of their initial values. In contrast to the sequence above, the positive solvatochromism and reduction in intensity follow the order of increasing solvent dielectric constant.

In the series of OPVs with vinyl cyanide moieties (**6−12**), two aspects are striking: The fluorescence quantum yield is much more sensitive to the polarity of the solvent, and the positive solvatochromism in the slightly polar chloroform is over 70% of the bathochromic shift found in acetonitrile. The effects of additional substituents are clearly visible: Electron-withdrawing trifluoromethyl substituents (**7**, **11**) diminish the red shift but greatly reduce the fluorescence intensity. Auxochromic methoxy groups produce a partial preservation of the fluorescence, particularly when the methoxy group is connected to the conjugated *o*- or *p*-positions of the terminal rings (**9**, **12**).

Table 2. Absorption and emission maxima [nm] of OPVs **1−12** in different solvents; CH = cyclohexane, DCM = dichloromethane, AN = acetonitrile, DIO = 1,4-dioxane, CLO = chloroform, ETH = ethanol

OPV	Abs. CH	Abs. DCM	log ε	Abs. AN	Fluo. CH	Fluo. DIO	Fluo. CLO	Fluo. DCM	Fluo. ETH	Fluo. AN
1	422	426	4.96	424	475	480	485	486	477	480
2	433	434	4.93	432	485	493	503	510	517	521
3	424	425	4.83	423	479	482	492	490	486	491
4	429	434	4.82	426	486	492	501	504	504	513
5	421	425	4.96	422	477	481	487	486	481	483
6	440	445	4.92	438	499	515	525	531	535	536
7	450	451	4.85	445	508	522	533	538	540	538
8	441	447	4.88	440	500	514	528	534	532	534
9	433	437	4.94	433	489	503	516	520	525	528
10	446	450	4.97	442	505	517	529	536	538	541
11	452	453	4.87	446	512	527	538	543	543	544
12	442	447	5.05	440	498	512	522	527	530	531

Table 3. Fluorescence quantum yields, and Stokes shifts in cyclohexane, solvatochromism and fluorescence intensities relative to solutions in cyclohexane (for solvent abbreviations see Table 1)

	Φ_F in CH	Stokes shift in CH [cm^{-1}]	CH/DIO [cm^{-1}] rel. I_f	CH/CLO [cm^{-1}] rel. I_f	CH/DCM [cm^{-1}] rel. I_f	CH/ETH [cm^{-1}] rel. I_f	CH/AN [cm^{-1}] rel. I_f
1	0.64	2644	219	434	485	57	219
			1.02	0.87	1.14	0.90	1.06
2	0.53	2476	335	738	1011	1276	1425
			1.23	0.88	0.83	0.70	0.64
3	0.65	2708	130	551	487	301	510
			0.92	0.89	0.78	0.77	0.67
4	0.37	2734	251	616	735	735	1083
			1.27	0.99	0.89	0.84	0.70
5	0.55	2789	174	430	388	174	260
			0.97	0.76	0.94	0.82	0.89
6	0.41	2687	388	992	1167	1308	1343
			0.68	0.55	0.44	0.26	0.14
7	0.37	2537	528	923	1098	1167	1098
			0.68	0.38	0.24	0.11	0.08
8	0.62	2676	544	1061	1273	1203	1273
			0.91	0.75	0.42	0.30	0.24
9	0.35	2645	569	1070	1219	1402	1511
			1.01	0.68	0.53	0.41	0.45
10	0.32	2620	460	898	1145	1215	1318
			0.73	0.44	0.38	0.20	0.14
11	0.37	2593	556	944	1115	1115	1149
			0.57	0.30	0.19	0.08	0.05
12	0.27	2544	549	923	1105	1212	1248
			1.15	0.77	0.61	0.46	0.43

The chromophore of OPV **13** differs from that of **12** in the positions of the cyano groups; they are shifted from the terminal styrene units to the centre of the molecule. The absorption spectrum has its maximum at 384 nm (CH_2Cl_2, log ε = 4.51) and the fluorescence peaks at 494 nm. The sensitivities of the absorption (384−396 nm) and emission (487−497 nm) towards solvent polarity are only small. Comparison of the low fluorescence intensity of **13** with those of **1−12** in solutions of similar optical density reveals a fluorescence quantum yield for **13** less than 10% of those displayed by **1−12**. This is in good agreement with the results obtained by Gill et al.[25b] for the OPVs **35** and **36** (Figure 2). Compound **35** is structurally related to **13**; the broad absorption peaks at 360 nm with a strong shoulder on the red side, and the emission maximum is at 502 nm with a fluorescence quantum yield of $\Phi_F = 0.04$. The isomer **36** (λ_{max} = 453 nm, $\lambda_{em,max}$ = 536 nm) is strongly fluorescent, with $\Phi_F = 0.7$. Upon exposure to daylight or NUV, **13** isomerises rapidly, unlike the photochemically fairly stable oligomers **1−12**.[26]

The influence of different substituents and substitution patterns on the reduction potential of the oligomers **1−12** in THF solution were studied by cyclic voltammetry (CV). The measured reduction potentials are shown in Table 4. As can be seen, the introduction of cyano groups onto the terminal rings of **1** results in an increase of 0.17 V in the

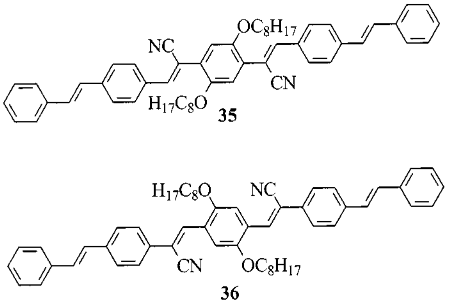


Figure 2. OPVs with cyano groups in the centre of the oligomer

reduction potential (**5**), whereas an exchange of terminal alkoxy and cyano moieties (**2**) produces a twofold increase in the reduction potential, independent of the position of the electron-withdrawing group on the ring (**2−4**). The electron affinities of compounds with vinyl cyanide segments, such as **6**, are substantially higher than those of the oligomers with benzonitrile structure and can be reduced by additional electron-donating groups (**9**, **12**) or further increased by electron-withdrawing groups (**7**, **10**, **11**). The effects of cyano substitution in the polymer PPV were studied by Brédas,[30] using quantum chemical calculations. The predicted increases in electron affinity are 0.18 V for the polymer with cyano groups on the benzene ring and 0.37 V for the polymer with vinyl cyanides.

Table 4. First reduction potentials of OPVs **1−12**

	R^1 (*para*)	R^2 (*meta*)	R^3 (*ortho*)	R^4 (vinyl)	$E^0_{1,\text{red}}$ [V]
1	OC_6H_{13}				−2.21
2	CN				−1.87
3		CN			−1.87
4			CN		−1.89
5	OC_6H_{13}	CN			−2.04
6				CN	−1.68
7		CF_3		CN	−1.54
8		OCH_3		CN	−1.65
9			OCH_3	CN	−1.83
10	Cl			CN	−1.60
11	CF_3			CN	−1.47
12	OCH_3			CN	−1.73

Discussion

The photoluminescence of cyano-substituted PPV has recently been measured in toluene/methanol and toluene/hexane mixed solvents, in order to distinguish between intermolecular and intramolecular photoexcitation.[31] Addition of the poor solvents to the good solvent toluene caused a red shift of the emission of cyano-substituted PPV and some loss of photoluminescence intensity, depending on the mixing ratio. Poor solvents tend to promote aggregation of the polymer, and the observed emission results from intermolecular excitations.

We have used a series of different solvents to study the emission behaviour of the highly soluble and strongly fluorescent, low molecular weight oligomers **1−12**. The individual substitution pattern (ring substitution versus vinyl cyanides, additional auxochromic groups) has distinct influences on the electronic spectra. Solvent effects on the absorption spectra are only small, a bathochromic shift of the absorption maximum being observed in going from cyclohexane to dichloromethane, with further increases in the dielectric constant of the solvent inducing a hypsochromic shift. This behaviour is more pronounced if the cyanide is bound to the vinylene linkage. Inverted solvatochromism had been observed for stilbazolium dyes and attributed to a change in the ground state electronic structure.[32] The ratio of the calculated dipole moments of the ground and excited states of these molecules changes from $\mu_g < \mu_e$ in nonpolar solvents to $\mu_g > \mu_e$ in polar solvents for the $\pi-\pi^*$ transition. In contrast to the absorption, the fluorescence is strongly dependent on the environment. Strong bathochromic shifts of emission are observed for OPVs with nitriles in the *o*- and *p*-positions and on the vinyl group (**2**, **4**, **6−12**), while cyanides in the *m*-position (**3**, **5**) induce only small red shifts. Such a dependence on the solvent dielectric constant can be attributed to the stabilisation of a charge transfer state by reorientation of the solvent molecules.[33] In the polar solvents, the emission of **2**, **4**, and **6−12** emanates from a state different from that in cyclohexane or dioxane. Though ring substitution (**2**, **4**) and vinyl substitution (**6−12**) of the OPVs with cyano groups both give rise to similar red shifts of the emission, their influences on the emission intensities differ considerably. Much higher sensitivity of the fluorescence intensity was found in vinyl-substituted OPVs than in ring-substituted OPVs. This response of the chromophore **6** towards polarity can be tuned by additional auxochromic or electron-withdrawing groups. Electron-donating alkoxy groups maintain the quantum yield remarkably (**8**, **9**, **12**), while electron-accepting trifluoromethyl groups further reduce the fluorescence by a factor of 2−3 (**7**, **11**). The latter groups promote charge transfer from the centre of the molecules to the terminal moieties. A strong reduction in fluorescence quantum yield arising from increased nonradiative decay in polar solvents has recently been reported for a distyrylbenzene with cyano groups on the vinylene linkages.[34] The consequences of the solvent polarity for the emission spectra are also of interest in the context of the use of OPVs with both electron-donating and electron-accepting groups in electrooptical devices. An influence of the strong electrical fields applied in light emitting diodes (e.g. 10^6 V/cm) on the luminescence properties is to be expected for push-pull substituted OPVs, as solvatochromism and electrochromism have the same origin: the influencing of the electron bands by electric fields.[35] The colour of the emitted light and, particularly, the luminescence efficiency of these excited molecules are strongly dependent on the local electrical fields of the rearranged solvent molecules or on external electrical fields.

Ring substitution with electron-accepting cyano groups is superior to vinyl substitution in terms of high fluorescence intensities in polar media.

Molecular Structures of OPVs 4 and 12

The solid-state structure of conjugated organic compounds has a powerful impact on electrical and optical properties. As the structure of polymers at the chain segment level is hard to characterise, conjugated oligomers are finding increasing interest as model compounds. They are often sufficiently crystalline to allow X-ray diffraction, offering a means to correlate molecular structure and solid-state properties. Hadziioannou et al.[25] have reported the molecular structure of the nonluminescent ($\Phi_F = 0.04$) oligomer **35**, possessing a wave-like shape with deviations of planarity of both rings and vinylene moieties of up to 5° and dihedral angles between the nitrile and the adjacent benzene ring of 11.7°, comparable to the dihedral angles of phenylenevinylene moieties in unsubstituted oligomers.[36]

Small single crystals of *o*-benzonitrile-terminated OPV **4** and of OPV **12**, with cyanovinylene groups, were obtained by crystallisation either from a cyclohexane/dichloromethane mixture (**4**) or from chloroform (**12**) and studied by X-ray diffraction. Though the formal structures of these molecules are very similar (the differences are the additional terminal methoxy groups and small shifts in the positions of the cyanides), the solid-state structures are distinctly different. Both molecules have a crystallographically imposed centre of inversion; the triclinic unit cell of **4** contains one molecule, while two oligomers **12** fill the monoclinic unit cell (Figure 3).

In the crystalline state of **12**, the phenylenevinylene units are packed in a "herringbone" arrangement; the molecules are coplanar, but the molecular axes are inclined with respect to the direct neighbours in the plane, while the neighbouring molecules in the adjacent layers are shifted about the length of a phenylenevinylene segment. The rigid and the flexible parts of the X-shaped OPV **12** are nearly coplanar, with an angle of 62° between the all-*trans*-configured heptyl segments of the side chains and the phenylenevinylene axis. The latter consists of 5 planar benzene rings (deviations from planarity: 1.2° or less) and four planar vinylene segments (C1−C4−C5−C6: 177.4°, C9−C12−C13−C14: 179.9°). Viewed from the centre of the molecule to the methoxy termini, the torsion angles between the planes of the benzene rings and the vinylene units are −165.0°, +172.3°, +166.5, and +168.6°, the slightly bent cyano group (N−C−C = 178.1°) is twisted about 12° out of the plane of the vinylene moiety. The terminal rings open dihedral angles of approximately 25° with the plane of the penultimate benzenes, whereas the rings of the central distyrylbenzene segment are close to be coplanar (ca. 5°). All vinylene bonds in the 1,4-divinylbenzene units are arranged in a *transoid* configuration, giving a rod-like shape to the basic chromophore.

In the crystalline state of OPV **4** (Figure 4), the axes of the conjugated units are parallel, with a face-to-face arrangement of the molecules in the adjacent layers. The octyloxy side chains are not coplanar with the chromophore; a plane containing the all-*trans*-configured heptyl segments and the molecular centre of inversion opens a dihedral angle of about 50° with the "plane" of the conjugated unit. The benzene rings and the vinylene units are essentially planar and the dihedral angles between them are substantially smaller than in **12**, viewed from the dialkoxybenzene to the benzonitrile units, torsion angles of 169.6, −174.1, 179.7, and −169.8° are found. The nitrile is linear (N−C−C = 179.3°) and coplanar with the benzene ring (178.9°). Again, the rings of the central distyrylbenzene unit are close to be coplanar (dihedral angle: 4.4°), whereas the planes of the penultimate rings and the benzonitriles are twisted about 9.9°. The vinylene bonds of the terminal styrene units in **4** are connected to the penultimate benzenes in an *s-cis* conformation relative to the vinylene moieties between the central and the penultimate rings, resulting in a slight "S"-type deviation of the conjugated system from linearity.

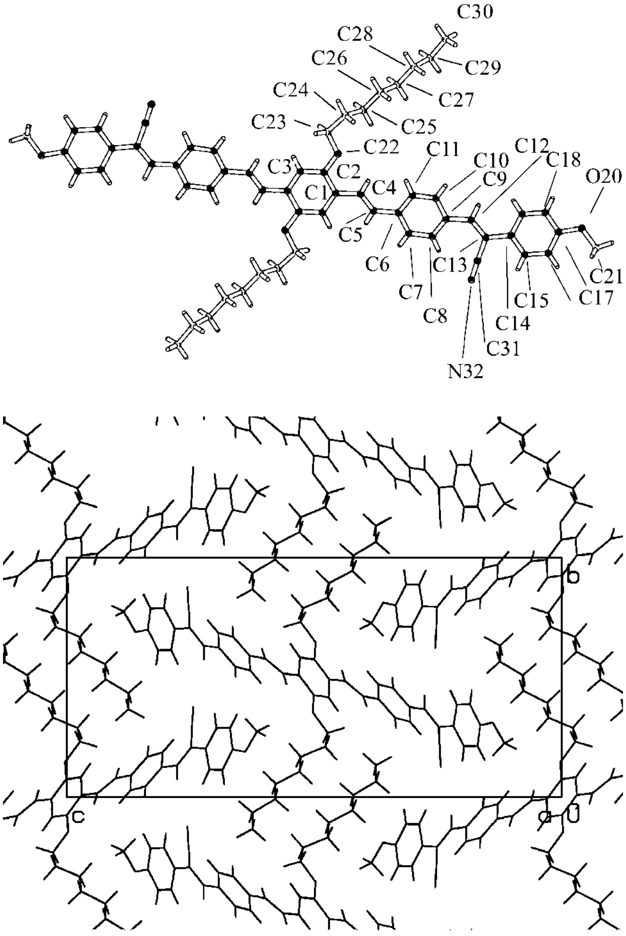


Figure 3. Molecular structure and packing of OPV **12**

Conclusion

Strongly fluorescent and highly soluble oligo(phenylenevinylene)s with five benzene rings and cyano groups on the terminal styrene moieties have been prepared by two double

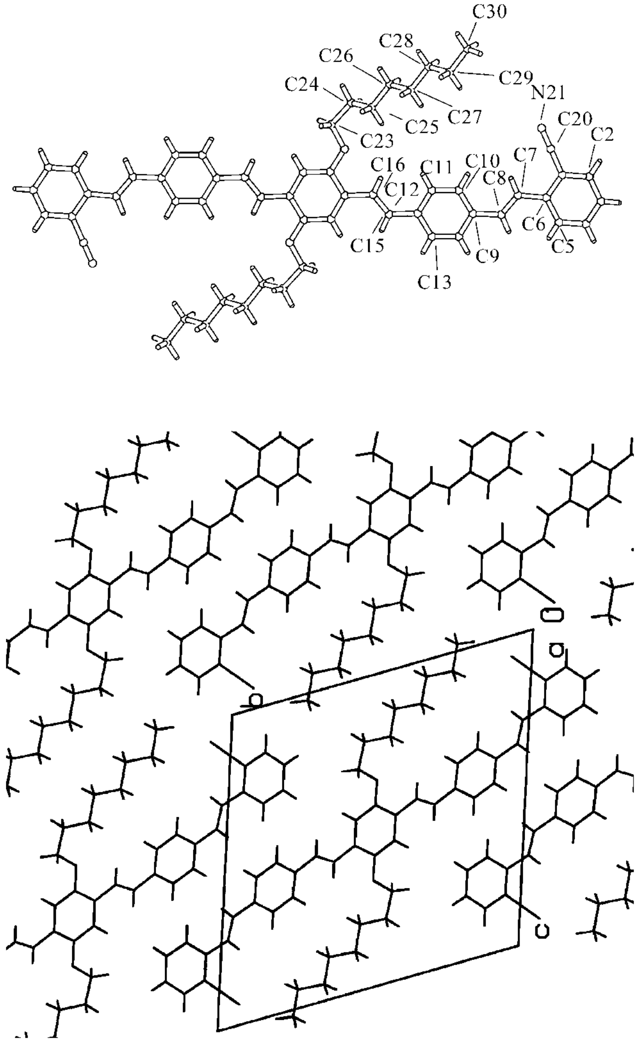


Figure 4. Molecular structure and packing of OPV **4**

olefination steps. A small degree of solvatochromism in the absorption and a strong responsiveness of the emission to the solvent dielectric constant indicate intramolecular charge transfer in the excited state. The fluorescence intensity of oligomers with vinyl cyanides is much more sensitive to the environment than that of ring-substituted chromophores. In the solid state, the structurally related OPVs **4** and **12** have comparable torsion angles between the conjugated segments, but the arrangement of the side chains and the packing are distinctively dependent on the substitution pattern.

Experimental Section

General: Melting points were determined with a Büchi melting point apparatus and are uncorrected. − IR spectra were obtained with a Beckman Acculab 4 in KBr or in neat form. − ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ with Bruker AC 200 and AM 400 instruments. − Mass spectra were obtained with Varian MAT 711 (EI-MS) and MAT 95 (FD-MS) instruments. − UV/Vis spectra were measured with a Perkin−Elmer Lambda 15 instrument. − Fluorescence spectra were obtained with a Perkin−Elmer LS50B, solvents for the electronic spectra were of spectroscopic grade, chloroform was treated with basic alumina before use. The fluorescence quantum yields were determined in aerated cyclohexane solution with optical densities between 0.005 and 0.01, quinine sulfate (Fluka, "for fluorescence") in 0.1 M H$_2$SO$_4$ was used as a reference (Φ_F = 0.577 at 350 nm).[38] − The elemental analyses were performed in the microanalytical laboratory of the Chemical Institute of the Johannes-Gutenberg-Universität, Mainz, Germany, eluent mixtures are v/v. − Chemicals were used as received; solvents were dried according to standard procedures and distilled. − Cyclic voltammetry was performed using a PG Stat 12 (Eco Chemie), glassy carbon as working electrode, Pt wire as counter-electrode and Ag/AgCl/LiCl/EtOH as a reference electrode. THF was used as solvent, tetrabutylammonium tetrafluoroborate as supporting electrolyte (0.1 M) and 10^{-3} M OPV, T = 30 °C, v = 100 mV/s. All measurements were calibrated vs. FeCp$_2$/FeCp$_2{}^+$ (+0.35 V vs. Ag/AgCl).[39]

X-ray Structure Determination of 4: Performed with an Enraf−Nonius Turbo-Cad4 equipped with rotating anode, using a transparent, yellow needle. Crystal data: $C_{56}H_{64}N_2O_2$, M = 793.06 g·mol^{-1}, 0.128 × 0.128 × 1.02 mm, triclinic, space group $P\bar{1}$, Cu-K_α, graphite monochromation: λ = 1.54180 Å, T = 296 K, unit cell dimensions: a = 423.92(6), b = 1668.82(15), c = 1697.46(23) pm, α = 71.333(10), β = 88.842(8), γ = 86.137(8)°, V = 1.1351(3) nm^3, Z = 1, $d_{\text{calcd.}}$ = 1.116 g·cm^{-3}, absorption μ = 0.53 mm^{-1}, Θ range for data collection 1.5−74°, index ranges $-5 \le h \le 0$, $-20 \le k \le 20$, $-21 \le l \le 21$. Number of reflections collected: 5265; independent reflections: 4613 (R_{int} = 0.0290). The structure was solved by direct methods (program SIR 92, refinement SHELXL-97).[40] Structure refinement by full-matrix least squares on 293 parameters, weighted refinement: $w = 1/[\sigma^2(F_0^2) + (0.0790 \times P)^2 + 0.15 \times P]$ with $P = [\max(F_0^2,0) + 2 \times F_c^2]/3$, hydrogen atoms adapted geometrically from difference Fourier synthesis with refinement, all non-hydrogen atoms improved with anisotropic temperature factors. Goodness-of-fit on S = 1.033, maximum change of parameters 0.000 × e.s.d, final R indices: R_1 = 0.0474, wR_2 = 0.1407, the final difference Fourier map showed minimum and maximum values of −0.15 and 0.27 e·Å^{-3}.

X-ray Structure Determination of 12: Performed with an Enraf−Nonius Turbo-Cad4 equipped with rotating anode, using a transparent, orange single crystal. Crystal data: $C_{58}H_{64}N_2O_4$, M = 853.11 g·mol^{-1}, 0.064 × 0.192 × 0.228 mm, monoclinic, space group $P2_1/c$, Cu-K_α, graphite monochromation: λ = 1.54180 Å, T = 296 K, unit cell dimensions: a = 669.33(7), b = 1335.69(4), c = 2723.0(4) pm, β = 90.233(6)°, V = 2.4791(4) nm^3, Z = 2, $d_{\text{calcd.}}$ = 1.143 g·cm^{-3}, absorption μ = 0.55 mm^{-1}, Θ range for data collection 1.5−74°, index ranges $0 \le h \le 81$, $0 \le k \le 16$, $-34 \le l \le 34$. Number of reflections collected: 5737; independent reflections: 5041 (R_{int} = 0.0443). The structure was solved by direct methods (program SIR 92, refinement SHELXL-97).[40] Structure refinement by full-matrix least squares on 310 parameters, weighted refinement: $w = 1/[\sigma^2(F_0^2) + (0.0615 \times P)^2 + 0.05 \times P]$ with $P = [\max(F_0^2,0) + 2 \times F_c^2]/3$, hydrogen atoms adapted geometrically from difference Fourier synthesis with refinement, all non-hydrogen atoms improved with anisotropic temperature factors. Goodness-of-fit on S = 1.009, maximum change of parameters 0.000 × e.s.d, final R indices: R_1 = 0.0574, wR_2 = 0.1565, the final difference Fourier map showed minimum and maximum values of −0.16 and 0.13 e·Å^{-3}.

1,4-Dioctyloxybenzene (14): A stirred mixture of hydroquinone (110.1 g, 1.0 mol), 1-bromooctane (424.9 g, 2.2 mol), potassium iodide (3 g), and Aliquat 336 (5 mL) in ethanol (600 mL) was purged with nitrogen and heated to reflux. Under exclusion of air, a solution of sodium hydroxide (88.0 g, 2.2 mol) in water (100 mL) was added over a period of 3 d to the boiling mixture, and heating and stirring were continued for a further 2 d. The mixture was cooled to room temperature and diluted with water (1.5 L), and the solid product was isolated by filtration and recrystallised from ethanol. Yield 273.9 g (82%); m.p. 56 °C (ref.[41]: 56 °C).

1,4-Bis(chloromethyl)-2,5-dioctyloxybenzene (15a): A solution of **14** (167.3 g, 0.5 mol) and hydrochloric acid (50 mL) in dioxane (650 mL) was cooled in an ice bath. The solution was saturated with gaseous hydrogen chloride and paraformaldehyde (30.0 g, 1.0 mol) was added. The stirred mixture was heated to reflux for 1 h, cooled in an ice bath and saturated with hydrogen chloride. H_2CO (15.0 g, 0.5 mol) was added and the mixture was heated to reflux for 1 h. The cooled mixture was diluted with 1 L water and filtered. The solid residue was dried in a dessicator and recrystallized from hexanes. Yield 146.2 g (68%); colourless needles; m.p. 72 °C. − ^1H NMR ($CDCl_3$): δ = 0.87 (t, 6 H, CH_3), 1.20−1.48 (m, 10 H, CH_2), 1.77 (quint, 4 H, β-CH_2), 3.96 (t, J = 6.4 Hz, 4 H, OCH_2), 4.62 (s, 4 H, CH_2Cl), 6.90 (s, 2 H, 3-H, 6-H). − EI MS (70 eV): m/z (%) = 430.4 (43) Cl_2 pattern [M^+], 206.3 (58) Cl_2 pattern [$M^+ - 2\ C_8H_{16}$], 43.4 (100)

Diethyl 4-[(Diethoxyphosphoryl)methyl]-2,5-bis(octyloxy)benzylphosphonate (16): A mixture of **15a** (107.5 g, 0.25 mol) in triethyl phosphite (124.5 g, 0.75 mol) was slowly heated until evolution of chloroethane started (ca. 170 °C). The temperature was maintained until the gas evolution had ceased, and the mixture was then heated to 185 °C for 30 min. The excess of triethyl phosphite was removed in vacuo, the oily residue was mixed with 50 mL of petroleum ether and the product crystallised upon standing at ambient temperature (2 weeks). Yield 154.8 g (98%); colourless solid; m.p. 47 °C. The preparation of **16** from **15b**[25b] followed the same procedure (T = 160 °C), with the reaction flask connected to a vertical condenser heated to 60 °C and the bromoethane being collected. Yield of **16** 154.7 g (98%). − IR (KBr): $\tilde{\nu}$ = 2980, 2900, 2840, 1500, 1460, 1410, 1385, 1265, 1205, 1030, 955, 638. − ^1H NMR ($CDCl_3$): δ = 0.76 (t, 6 H, CH_3, oct), 1.4−1.05 (m, 32 H, CH_2 oct, CH_3 eth), 1.65 (quint, J = 7.2 Hz, 4 H, β-CH_2 oct), 3.10 (d, $^2J_{(H,\ P)}$ = 20.2 Hz, 4 H, aryl-CH_2), 3.80 (t, J = 6.6 Hz, 4 H, OCH_2 oct), 3.91 (m, 8 H, OCH_2 eth), 6.81 (d, $^4J_{(H,\ P)}$ = 1.4 Hz, 1 H, 3-H, 6-H, ar). − ^{13}C NMR ($CDCl_3$): δ = 13.9 (CH_3, oct), 16.2 (CH_3, eth), 26.1 (d, $^1J_{(C,\ P)}$ = 139.5 Hz, aryl-CH_2), 22.5, 26.0, 29.1, 29.2, 29.3, 31.7 (CH_2 oct), 61.7 (OCH_2 eth), 68.8 (OCH_2 oct), 114.8 (C-3, C-6, ar), 119.3 (d, $^2J_{(C,\ P)}$ = 2.3 Hz, C-1, C-4, ar), 150.2 (C-2, C-5, ar). − EI MS (70 eV): m/z (%) = 634.6 (100) [M^+], 522 (10) [$M^+ - C_8H_{16}$]. − $C_{32}H_{60}O_8P_2$ (631.77): calcd. C 60.55, H 9.53; found C 60.58, H 9.48.

4-[(*E*)-2-{4-[(*E*)-2-(4-Formylphenyl)ethenyl]-2,5-bis(octyloxy)-phenyl}ethenyl]benzaldehyde (18): Dry THF (150 mL) and KO*t*Bu (25.8 g, 0.23 mol) were placed in a three-necked, round-bottomed flask, together with 18-crown-6 (0.7 g). A connected dropping funnel was charged with aldehyde **17** (43.7 g, 0.21 mol) and bis(phosphonate) **16** (63.5 g, 0.10 mol), dissolved in dry THF (15 mL). After the solutions had been purged with argon, the mixture was added slowly (30 min) to a mechanically stirred solution of the base at room temperature and stirring was continued for 2 h. The reaction was quenched by addition of crushed ice/hydrochloric acid and stirred for 12 h (pH ≈ 2). The mixture was diluted with water and the precipitate was collected by filtration, washed with water, water/ethanol (1:1) and water and dried. Purification was done by double recrystallisation from dichloromethane/ethanol and chromatography of the residual product in the mother liquors on silica gel with toluene/ethyl acetate. Yield 33.9 g (57%); bright orange to red powder; m.p. 138 °C. − IR (KBr): $\tilde{\nu}$ = 3035, 2920, 2848, 1685, 1588, 1557, 1487, 1461, 1416, 1301, 1205, 1163, 963, 812. − ^1H NMR ($CDCl_3$): δ = 0.83 (t, 6 H, CH_3), 1.63−1.20 (m, 20 H, CH_2), 1.85 (quint, J = 6.4 Hz, 4 H, β-CH_2), 4.07 (t, J = 7.5 Hz, 4 H, OCH_2), 7.11 (s, 2 H, 3-H, 6-H), 7.19 (d, J = 17.6 Hz, 2 H, 1-H, ethen), 7.58 (d, J = 17.6 Hz, 2 H, 2-H, ethen), 7.66 (d, J = 7.8 Hz, 4 H, 2′-H, 6′-H, ar), 7.86 (d, J = 7.8 Hz, 4 H, 3′-H, 5′-H, ar), 9.97 (2 H, CHO). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6, 26.3, 29.3, 29.4, 29.4, 31.7 (CH_2), 69.6 (OCH_2), 111.0 (C-3, C-6), 126.9 (6 C), 127.0 (2 C), 128.0 (2 C), 130.2 (CH), 135.3 (2 C), 144.3 (2 C), 151.5 (C-2, C-5), 191.5 (CHO). − FD MS: m/z (%) = 595.2 (17) [M^+], 567.1 (15) [$M^+ - CO$], 539.1 (5) [$M^+ - 2\ CO$], 43.3 (100). − $C_{40}\ H_{50}\ O_4$ (594.835): calcd. C 80.77, H 8.47; found C 80.87, H 8.54.

Diethyl [4-(Hexyloxy)benzyl]phosphonate (19): This compound was prepared according to the literature.[42]

Diethyl (2-Cyanobenzyl)phosphonate (20),[43] Diethyl (3-Cyanobenzyl)phosphonate (21),[44] and Diethyl (4-Cyanobenzyl)phosphonate (23)[45]: These compounds were prepared from the commercially available chloromethyl benzonitriles and triethyl phosphite according to the procedures given above.

Diethyl [3-Cyano-4-(hexyloxy)benzyl]phosphonate (22): A mixture of NBS (17.8 g, 0.10 mol), compound **34** (23.9 g, 0.11 mol), AIBN (250 mg), and dry CCl_4 (400 mL) was refluxed for 5 h. The cooled mixture was filtered and the solvent evaporated. The crude bromide was added to triethyl phosphite (20.0 g, 0.12 mol) and the stirred mixture was heated to 170 °C. When the evolution of ethyl bromide had ceased, the residual triethyl phosphite was distilled off and the oily residue was purified by column chromatography on silica gel (20 × 12 cm), using toluene with increasing ethyl acetate content as eluent. Yield 16.2 g (46%); yellowish oil. − IR (neat):$\tilde{\nu}$ = 2975, 2920, 2850, 2224, 1600, 1493, 1477, 1385, 1290, 1260, 1160, 1050, 1028, 965, 850, 800, 735. − ^1H NMR ($CDCl_3$): δ = 0.81 (m, 3 H, CH_3), 1.10−1.50 (m, 12 H, CH_2 hex, CH_3 eth), 1.78 (quint, J = 7 Hz, 2 H, β-CH_2), 2.98 (d, $^2J_{(H,\ P)}$ = 21 Hz, 2 H, aryl-CH_2), 3.90−4.05 (m, 6 H, OCH_2), 6.84 (d, J = 9.2 Hz, 1 H, 5-H), 7.33−7.43 (m, 2 H, 2-H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 13.9 (CH_3 hex), 16.3 (d, $^4J_{(H,\ P)}$ = 6.4 Hz, CH_3 eth), 22.4, 25.4, 28.8, 31.3 (CH_2 hex), 32.3 (d, $^1J_{(C\text{-}P)}$ = 138 Hz, aryl-CH_2), 62.2 (d, $^2J_{(C,P)}$ = 6.5 Hz, OCH_2 eth), 69.1 (OCH_2 hex), 102.0 (d, $^4J_{(C,\ P)}$ = 2.5 Hz, C-3), 112.4 (d, $^4J_{(C,\ P)}$ = 3.2 Hz, C-4), 116.1 (CN), 124.2 (d, $^2J_{(C,\ P)}$ = 8.8 Hz, C-1), 134.4 (d, $^3J_{(C,\ P)}$ = 7.2 Hz), 135.6 (d, $^3J_{(C,\ P)}$ = 6.4 Hz) (C-2, C-6), 159.7 (d, $^5J_{(C,\ P)}$ = 2.3 Hz, C-4). − FD MS: m/z (%) = 353.3 [M^+]. − $C_{18}H_{28}NO_4P$ (353.393): calcd. C 61.18, H 7.99, N 3.96; found C 60.98, H 7.91, N 3.98.

4-{(*E*)-2-[4-(Hexyloxy)phenyl]ethenyl}benzaldehyde (31): This preparation was performed using **17** (2.1 g, 0.01 mol), **19** (3.3 g, 0.01 mol), and KO*t*Bu (1.2 g, 0.01 mol) in THF (50 mL), according to the procedure described for **18**. Yield 1.9 g (62%); colourless solid; m.p. 168 °C. − IR (KBr): $\tilde{\nu}$ = 2950, 2922, 2860, 1680, 1590, 1545, 1505, 1465, 1300, 1250, 1218, 1171, 1160, 1030, 964, 830. − ^1H NMR ($CDCl_3$): δ = 0.9 (t, 3 H, CH_3), 1.25−1.58 (m, 6 H, CH_2), 1.77 (quint, J = 6.5 Hz, 2 H, β-CH_2), 3.96 (t, J = 7 Hz, 2 H, OCH_2), 6.91 (d, J = 8 Hz, 2 H, 3′-H, 5′-H), 6.98 (d, J = 16 Hz, 1 H, olef. H), 7.19 (d, J = 16 Hz, 1 H, olef. H), 7.46 (d, J = 8 Hz, 2 H, 2′-H, 6′-H), 7.61 (d, J = 7.6 Hz, 2 H, 2-H, 6-H), 7.83 (d, J = 7.6 Hz, 2 H, 3-H, 5-H), 9.99 (s, 1 H, CHO). − ^{13}C NMR ($CDCl_3$):

δ = 14.0 (CH_3), 22.6, 25.7, 29.2, 31.6 (CH_2), 68.2 (OCH_2), 114.9 (CH), 125.0 (CH), 126.6 (2 C, CH), 128.4 (2 C, CH), 129.1 (C_q), 130.2 (2 C, CH), 131.9 (CH), 135.0, 143.9 (C_q), 159.7 (C−O), 191.6 (CHO). − EI MS (70 eV): *m/z* (%) = 308.3 (80) [M^+], 223.9 (100) [$M^+ - C_6H_{12}$]. − $C_{21}H_{24}O_2$ (308.420): calcd. C 81.78, H 7.84; found C 81.53 H 7.61

2-(Hexyloxy)-5-methylbenzonitrile (34): Anhydrous sodium acetate (9.3 g, 0.11 mol) was added to a solution of 4-(hexyloxy)toluene (19.2 g, 0.10 mol) in glacial acetic acid (70 mL). The mixture was stirred mechanically and a solution of bromine (5.1 mL, 0.10 mol) in acetic acid (15 mL) was added dropwise, the temperature being kept below 35 °C by external cooling. After the bromine had been consumed, the mixture was diluted with water (200 mL), the organic layer was separated and the aqueous phase was extracted with hexanes (3 × 50 mL). The pooled organic solutions were washed with water (3 × 100 mL) and a saturated aqueous solution of $NaHCO_3$ (3 × 100 mL) and brine (50 mL), and dried with $CaCl_2$. The solvent was evaporated. The residue was dissolved in dry DMF (70 mL), CuCN (14.5 g, 0.15 mol) was added and the mixture was heated to 150 °C and stirred for 36 h. The cooled mixture was poured into aqueous ammonia (25%) (200 mL) and stirred for 4 h. The blue solution was extracted with toluene (3 × 50 mL) and the pooled organic solutions were washed with water (2 × 100 mL) and brine (100 mL) and dried with $MgSO_4$. The solvent was evaporated and the crude product was purified by chromatography on silica gel (20 × 7 cm), with petroleum ether (40−70 °C) and a gradually increasing content of ethyl acetate. Yield 13.9 g (64%); yellowish oil. − IR (neat): ṽ = 2940, 2910, 2848, 2220, 1599, 1490, 1458, 1283, 1260, 1117, 1018, 810. − ^1H NMR ($CDCl_3$): δ = 0.89 (t, *J* = 5.5 Hz, 3 H, CH_3), 1.25−1.58 (m, 6 H, CH_2), 1.81 (quint, *J* = 7 Hz, 2 H, β-CH_2), 2.28 (s, 3 H, aryl-CH_3), 4.02 (t, *J* = 6 Hz, 2 H, OCH_2), 6.82 (d, *J* = 8.0 Hz, 1 H, 3-H), 7.28 (m, 2 H, 4-H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 20.0, 22.6, 25.6, 28.9, 31.5, (CH_2, CH_3), 69.1 (OCH_2), 101.6 (C-1), 112.3 (C-3), 116.6 (CN), 130.0 (C-5), 133.6, 134.9 (C-4, C-6), 158.8 (C-2). − EI MS (70 eV): *m/z* (%) = 217.1 (7) [M^+], 133.2 (100) [$M^+ - C_6H_{12}$], 42.4 (42). − $C_{14}H_{19}NO$ (217.307): calcd. C 77.38, H 8.81, N 6.45; found C 77.12, H 8.92, N 6.15.

General Procedure for the Synthesis of OPVs 1−5 by Horner−Wittig Olefination: A dried, three-necked, round-bottomed flask was fitted with a magnetic stirring bar and a dropping funnel. The flask was charged with KO*t*Bu (336 mg, 3.0 mmol), 18-crown-6 (100 mg) and abs. THF (15 mL), the funnel with a solution of **18** (594 mg, 1.0 mmol) and a phosphonate (**19−23**) (2.1 mmol) in abs. THF (35 mL). The apparatus was evacuated and flushed with argon (3 ×) and the starting materials were added to the base while stirring at ambient temperature. The mixtures immediately turned dark green and became fluorescent. The reaction was monitored by TLC and quenched with water (15 mL) (reaction time 20 min to 4 h). The bulk of the solvent was stripped off, the residue diluted with water. Solid products were filtered, **4** and **5** were extracted with dichloromethane. Purification of **4** and **5** was done by chromatography on silica gel with toluene, **1−3** were recrystallised from chloroform/methanol. For purposes of comparison, the carbon and hydrogen atoms are numbered according to Figure 5.

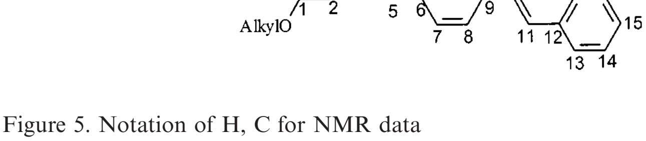


Figure 5. Notation of H, C for NMR data

1,4-Bis[(*E*)-2-(4-{(*E*)-2-[4-(hexyloxy)phenyl]ethenyl}phenyl)ethenyl]-2,5-bis(octyloxy)benzene (1): Yield 0.76 g (81%); light yellow powder; m.p. 164 °C. − IR (KBr): ṽ = 3010, 2905, 2845, 1600, 1505, 1460, 1415, 1248, 1200, 1170, 967, 848, 828. − ^1H NMR: δ = 0.89 (m, 12 H, CH_3), 1.22−1.70 (m, 32 H, CH_2), 1.70−1.95 (m, 8 H, β-CH_2), 3.95 (t, *J* = 6.6 Hz, 4 H, OCH_2 hex), 4.06 (t, *J* = 6 Hz, 4 H, OCH_2 oct), 6.89 (d, *J* = 8 Hz, 4 H, 14-H, 16-H), 6.96 (d, *J* = 16 Hz, 2 H, vin), 7.07 (d, *J* = 16 Hz, 2 H, vin), 7.11 (s, 2 H, 2-H), 7.12 (d, *J* = 16 Hz, 2 H vin), 7.40−7.54 (m, 14 H, 7-H, 8-H, 13-H, 17-H, CH vin). − ^{13}C NMR: δ = 14.0, 14.1 (CH_3 hex, oct), 22.6, 22.7, 25.7, 26.3, 29.3, 29.4, 29.5, 29.6, 31.6, 31.9 (CH_2 hex, oct), 68.1, 69.6 (OCH_2 hex, oct), 110.6 (C-2), 114.8 (C-14, C-16), 123.2, 126.1, 127.0, 128.1, 128.4, 130.0, 136.9, 137.0 (CH, C_q ar, vin), 151.2 (C-1), 158.9 (C-15). − FD MS: *m/z* (%) = 943.4 (100) [M^+], 471.7 (4) [M^{2+}]. − $C_{66}H_{86}O_4$ (943.387): calcd. C 84.03, H 9.19; found C 84.14, H 9.06.

4-[(*E*)-2-{4-[(*E*)-2-{4-[(*E*)-2-{4-[(*E*)-2-(4-Cyanophenyl)ethenyl]-phenyl}ethenyl]-2,5-bis(octyloxy)phenyl}ethenyl]phenyl}ethenyl]-benzonitrile (2): Yield 0.66 g (83%); yellow needles; m.p. 208 °C (*i*PrOH/$CHCl_3$). − IR (KBr): ṽ = 3010, 2908, 2840, 2220, 1590, 1582, 1502, 1480, 1453, 1408, 1248, 1195, 1019, 957, 850, 830, 820. − ^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 6 H, CH_3), 1.25−1.45 (m, 20 H, CH_2), 1.56 (quint, *J* = 7.5 Hz, 4 H, CH_2), 1.87 (quint, *J* = 7.5 Hz, 4 H, β-CH_2), 4.07 (t, *J* = 6 Hz, 4 H, OCH_2), 7.06 (d, *J* = 16.4 Hz, 2 H, vin), 7.11 (s, 2 H, 2-H), 7.13 (d, *J* = 16 Hz, 2 H, vin), 7.19 (d, *J* = 16.4 Hz, 2 H, vin), 7.53 (d, *J* = 16 Hz, 2 H, vin), 7.52 (AA′BB′, 8 H, 7-H, 8-H), 7.59 (AA′BB′, 8 H, 13-H, 14-H, 16-H, 17-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.3, 29.3, 29.4, 29.5, 31.8 (CH_2), 69.6 (OCH_2), 110.5 (C-15), 110.7 (C-2), 119.0 (CN), 124.1, 126.4 (CH vin), 126.8, 127.0, 127.3 (CH ar, C-7, C-8, C-13, C-17), 138.3, 132.0 (CH vin), 132.5 (CH ar, C-14, C-16), 135.4, 138.5, 141.9 (C_q, C-3, C-6, C-9), 151.3 (C_q, C-1). − FD MS: *m/z* (%) = 792.7 (100) [M^+]. − $C_{56}H_{60}N_2O_2$ (793.088): calcd. C 84.81, H 7.63, N 3.53; found C 84.60, H 7.79, N 3.51.

2-[(*E*)-2-{4-[(*E*)-2-{4-[(*E*)-2-{4-[(*E*)-2-(3-Cyanophenyl)ethenyl]-phenyl}ethenyl]-2,5-bis(octyloxy)phenyl}ethenyl]phenyl}ethenyl]-benzonitrile (3): Yield 0.61 g (77%); dark orange crystals; m.p. 168 °C. − IR (KBr): ṽ = 3010, 2950, 2905, 2846, 2222, 1610, 1580, 1515, 1495, 1470, 1435, 1217, 1077, 1033, 1974, 820, 691. − ^1H NMR: δ = 0.89 (t, 6 H, CH_3), 1.20−1.65 (m, 20 H, CH_2), 1.88 (quint, *J* = 6.8 Hz, 4 H, β-CH_2), 4.08 (t, *J* = 6.6 Hz, 4 H, OCH_2), 7.06 (d, *J* = 16 Hz, 2 H, CH vin), 7.12 (s, 2 H, 2-H), 7.13−7.21 (m, 4 H, CH vin, ar), 7.40−7.58 (m, 14 H, 7-H, 8-H, CH ar, vin), 7.71 (d, *J* = 7.8 Hz, 2 H, 15-H), 7.78 (s, 2 H, 13-H). − ^{13}C NMR: δ = 14.1 (CH_3), 22.7, 26.4, 29.4, 29.5, 29.5, 31.9 (CH_2), 69.6 (OCH_2), 110.7 (C-14), 113.0 (C-2), 118.8 (CN), 127.0, 127.2 (C-7, C-8), 124.0, 125.8, 128.2, 129.0, 129.5, 129.8, 130.5, 130.6, 131.0, 135.5, 138.3, 138.7 (CH, C_q ar, vin), 151.2 (C-1). − FD MS: *m/z* (%) = 793.4 (100) [M^+]. − $C_{56}H_{60}N_2O_2$ (793.088): calcd. C 84.81, H 7.63 N 3.53; found C 84.66, H 7.38, N 3.19.

2-[(*E*)-2-{4-[(*E*)-2-{4-[(*E*)-2-{4-[(*E*)-2-(2-Cyanophenyl)ethenyl]-phenyl}ethenyl]-2,5-bis(octyloxy)phenyl}ethenyl]phenyl}ethenyl]-benzonitrile (4): Yield 0.57 g (72%); yellow powder; m.p. 188 °C. − IR (KBr): ṽ = 3017, 2910, 2840, 2222, 1620, 1582, 1503, 1485, 1465, 1418, 1338, 1200, 1065, 960, 840, 808, 755. − ^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.3 Hz, 6 H, CH_3), 1.22−1.65 (m, 20 H,

CH_2), 1.91 (quint, J = 6.8 Hz, 4 H, β-CH_2), 4.07 (t, J = 6 Hz, 4 H, OCH_2), 7.13 (s, 2 H, 2-H), 7.15 (d, J = 16.2 Hz, 2 H, vin), 7.26 (d, J = 16 Hz, 2 H, vin), 7.31 (t, J = 7.8 Hz, 2 H, 14-H), 7.44 (d, J = 16.2 Hz, 2 H, vin), 7.47−7.62 (m, 12 H, 6-H, 7-H, 15-H, CH vin), 7.64 (d, J = 8 Hz, 2 H, 17-H), 7.79 (d, J = 8 Hz, 2 H, 13-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.3, 29.4, 29.5, 29.5, 31.8 (CH_2), 69.6 (OCH_2), 110.7, 111.2, 123.6, 124.2, 125.2, 127.0, 127.5 (CH), 118.0 (CN), 128.2, 132.7, 133.0, 133.2, 135.2, 138.6, 140.7 (CH, C_q), 151.3 (C-1). − FD MS: m/z (%) = 793.0 (100) [M^+], 396.5 (1) [M^{2+}]. − $C_{56}H_{60}N_2O_2$ (793.088): calcd. C 84.81, H 7.63, N 3.53; found C 84.76, H 7.56, N 3.48.

5-{(*E*)-2-[4-{(*E*)-2-[4-{(*E*)-2-[4-{(*E*)-2-[3-Cyano-4-(hexyloxy)phenyl]ethenyl}phenyl]ethenyl}-2,5-bis(octyloxy)phenyl]ethenyl}phenyl]ethenyl}-2-(hexyloxy)benzonitrile (5): Yield 0.73 g (74%); light orange powder; m.p. 166 °C. − IR (KBr): ṽ = 3010, 2910, 2840, 2220, 1595, 1500, 1463, 1413, 1274, 1115, 1013, 954, 817, 730. − ^{1}H NMR ($CDCl_3$): δ = 0.90 (m, 12 H, CH_3), 1.20−1.62 (m, 32 H, CH_2), 1.85 (m, 8 H, β-CH_2), 4.07 (m, 8 H, OCH_2), 6.94 (d, J = 8 Hz, 2 H, 16-H), 6.98 (m, 4 H, vin), 7.12 (s, 2 H, 2-H), 7.13 (d, J = 16 Hz, 2 H, vin), 7.48 (m, 10 H, 7-H, 8-H, CH vin), 7.63 (dd, J = 8.2 Hz, 1 H, J' = 1.8 Hz, 17-H), 7.67 (d, J = 1.8 Hz, 1 H, 13-H). − ^{13}C NMR ($CDCl_3$): δ = 13.9, 14.0 (CH_3), 22.5, 22.6, 25.5, 26.3, 28.9, 29.3, 29.4, 29.5, 31.4, 31.8 (CH_2), 69.4, 69.7 (OCH_2), 102.7 (C-14), 110.8, 112.6 (C-2, C-16), 116.2 (CN), 126.8, 126.9 (C-7, C-8), 123.7, 125.9, 127.0, 128.3, 128.5, 130.6, 131.4, 132.0, 136.0, 137.9 (CH, C_q ar, vin), 151.3 (C-1), 160.1 (C-15). − FD MS: m/z (%) = 993.2 (100) [M^+], 497.1 (6) [M^{2+}]. − $C_{68}H_{84}N_2O_4$ (993.406): calcd. C 82.21, H 8.52, N 2.82; found C 81.87, H 8.46, N 2.78.

General Procedure for the Synthesis of OPVs 6−2 by Knoevenagel Condensation: Under argon, solid KO*t*Bu (224 mg, 2.0 mmol) was added to a stirred solution of **18** (594 mg, 1.0 mmol) and benzyl cyanide (**24**−**30**) (2.1 mmol) in abs. THF (20 mL) and *tert*-butyl alcohol (15 mL). Upon addition of the base, the mixture turned dark and spontaneous precipitation of the red to dark-red OPVs (**10**, **11**, **12**) occurred. When the reaction was complete (15 min to 3 h), the mixture was poured into water (100 mL) and either the precipitate was collected (**7**, **10**−**12**) or the compounds (**6**, **8**, and **9**) were isolated by extraction with chloroform (3 × 50 mL) and the pooled organic solutions were washed with water and brine and dried with Na_2SO_4. Purification was done by recrystallisation from chloroform/isopropyl alcohol (**6**, **7**, **10**−**12**) or chromatography on silica gel, using toluene as eluent (**8**, **9**).

(2*Z*)-3-{4-[(*E*)-2-{4-[(*E*)-2-{4-[(*Z*)-2-Cyano-2-phenylethenyl]phenyl}ethenyl]-2,5-bis(octyl oxy)phenyl}ethenyl]phenyl}-2-phenyl-2-propenenitrile (6): Yield 0.51 g (64%); red powder, m.p. 156 °C. − IR (KBr): ṽ = 2920, 2850, 2215, 1580, 1505, 1490, 1422, 1338, 1258, 1200, 966, 902, 860. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (m, 6 H, CH_3), 1.20−1.70 (m, 20 H, CH_2), 1.90 (quint, J = 7.5 Hz, 4 H, β-CH_2), 4.09 (t, J = 6.0 Hz, 4 H, OCH_2), 7.13 (s, 2 H, 1-H), 7.17 (d, J = 16 Hz, 2 H, vin), 7.38 (tt, J = 8 Hz, 2 H, 15-H), 7.44 (m, 4 H, 14-H), 7.52 (s, 2 H, 10-H), 7.58 (d, 2 H, vin), 7.60 (d, J = 8 Hz, 2 H, 7-H), 7.67 (dt, J = 6.8 Hz, 2 H, 13.H), 7.89 (d, J = 8 Hz, 4 H, ar). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.3, 29.3, 29.4, 29.5, 31.9 (CH_2), 69.6 (OCH_2), 110.6 (C-2), 110.7 (C-12), 118.3 (CN), 126.0, 126.9, 129.1, 129.9 (C-7, C-8, C-12, C-13), 125.5, 127.9, 141.7 (CH), 129.1, 132.6, 134.7, 140.3 (C_q), 151.3 (C-1), 1 CH signal missing. − FD MS: m/z (%) = 793.0 (100) [M^+], 396.6 (4) [M^{2+}]. − $C_{56}H_{60}N_2O_2$ (793.088): calcd. C 84.81, H 7.63, N 3.53 found C 84.31, H 7.73, N 3.16.

(2*Z*)-3-[4-{(*E*)-2-[4-{(*E*)-2-[4-{(*Z*)-2-Cyano-2-[3-(trifluoromethyl)phenyl]ethenyl}phenyl]ethenyl}-2,5-bis(octyloxy)phenyl]ethenyl}phenyl]-2-[3-(trifluoromethyl)phenyl]-2-propenenitrile (7): Yield 0.73 g (79%); dark orange crystals; m.p. 203 °C. − IR (KBr): ṽ = 2920, 2845, 2217, 1578, 1330, 1240, 1114, 1078, 960, 690. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 6 H, CH_3), 1.20−1.65 (m, 20H, CH_2), 1.90 (quint, J = 6.5 Hz, 4 H, β-CH_2), 4.08 (t, J = 7 Hz, 4 H, OCH_2), 7.14 (s, 2 H, 2-H), 7.19 (d, J = 16 Hz, 2 H, vin), 7.54−7.68 (m, 12 H, CH vin, ar), 7.84−7.93 (m, 8 H, CH vin, ar). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.3, 29.3, 29.4, 29.5, 31.8 (CH_2), 69.6 (OCH_2), 109.1 (C-11), 110.7 (C-2), 117.8 (CN), 122.7 (m), 125.6 (m), 125.9, 127.9, 129.3, 129.7, 132.1, 135.6, 140.9, 143.2 (CH, C_q ar, vin), 127.0, 130.1 (C-7, C-8), 151.4 (C-1), 3 signals missing due to intensive C,F coupling. − FD MS: m/z (%) = 928.8 (100) [M^+], 464.4 (4) [M^{2+}]. − $C_{58}H_{58}F_6N_2O_2$ (929.084): calcd. C 74.98, H 6.29, N 3.02; found C 75.02, H 6.27, N 3.17.

3-{4-[(*E*)-2-{4-[(*E*)-2-{4-[(*Z*)-2-Cyano-2-(3-methoxyphenyl)ethenyl]phenyl}ethenyl]-2,5-bis(octyloxy)phenyl}ethenyl]phenyl}-2-(3-methoxyphenyl)-2-propenenitrile (8): Yield 0.61 g (72%); red solid; m.p. 148 °C. − IR (KBr): ṽ = 2910, 2840, 2208, 1585, 1482, 1455, 1415, 1275, 1203, 1042, 960, 850. − ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 6 H, CH_3), 1.25−1.63 (m, 20 H, CH_2), 1.90 (quint, J = 6.5 Hz, 4 H, β-CH_2), 3.86 (s, 6 H, OCH_3), 4.08 (t, J = 6.5 Hz, 4 H, OCH_2), 6.93 (ddd, J = 7.7 Hz, 1 H, 15-H), 7.13 (s, 2 H, 2-H), 7.17 (d, J = 16 Hz, 2 H, vin), 7.20 (m, 1 H, 13-H), 7.29 (m, 2 H, 17-H), 7.36 (dd, J = J' = 7.5 Hz, 2 H, 16-H), 7.51 (s, 2 H, 10-H), 7.59 (d, 2 H, vin), 7.62 (d, J = 8 Hz, 4 H), 7.90 (d, J = 8 Hz, 4 H, 8-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.3, 29.3, 29.4, 29.5, 31.8 (CH_2), 55.5 (OCH_3), 69.6 (OCH_2), 110.5, 110.7, 111.6, 114.7, 118.4 (CN), 125.5, 126.9 (2 ×), 128.0, 129.9 (2 ×), 130.1, 132.6, 136.1, 140.4, 141.9 (CH, C_q), 151.4, 160.1 (C−O). − FD MS: m/z (%) = 854.5 (100) [M^+], 427.0 (38) [M^{2+}]. − $C_{58}H_{64}N_2O_4$ (853.140): calcd. C 81.65, H 7.56, N 3.28; found C 81.59, H 7.57, N 3.18.

(2*Z*)-3-{4-[(*E*)-2-{4-[(*E*)-2-{4-[(*Z*)-2-Cyano-2-(2-methoxyphenyl)ethenyl]phenyl}ethenyl]-2,5-bis(octyloxy)phenyl}ethenyl]phenyl}-2-(2-methoxyphenyl)-2-propenenitrile (9): Yield 0.49 g (57%); dark yellow powder; m.p. 190 °C. − IR (KBr): ṽ = 2910, 2840, 2210, 1590, 1480, 1450, 1255, 1195, 1020, 962. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 6 H, CH_3),1.22−1.60 (m, 24 H, CH_2), 1.88 (quint, J = 6.5 Hz, 4 H, β-CH_2), 3.91 (s, 6 H, OCH_3), 4.08 (t, J = 6.5 Hz, 4 H, OCH_2), 6.93−7.06 (m, 4 H, 14-H, 16-H), 7.13 (s, 2 H, 2-H), 7.16 (d, J = 16 Hz, 2 H, vin), 7.31−7.45 (m, 6 H, 15-H, 17-H, CH vin), 7.57 (d, J = 16 Hz, 2 H, CH vin), 7.59 (d, J = 8 Hz, 4 H, 7-H), 7.88 (d, J = 8 Hz, 4 H, 8-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.6, 26.3, 29.3, 29.4, 29.5, 31.8 (CH_2), 55.8 (OCH_3), 69.7 (OCH_2), 108.1, 110.9, 111.7, 118.3 (CN), 121.1, 125.0, 125.3, 126.8 (2 ×), 127.1, 128.1, 129.7 (2 ×), 129.9, 130.4, 133.1, 140.1, 145.4 (CH, C_q), 151.4, 157.1 (C−O). − FD MS: m/z (%) = 1707.0 (9) [M_2^+], 853.5 (100) [M^+], 426.8 (11) [M^{2+}]. − $C_{58}H_{64}N_2O_4$ (853.140): calcd. C 81.65, H 7.56, N 3.28; found C 81.59, H 7.57, N 3.18.

(2*Z*)-2-(4-Chlorophenyl)-3-{4-[(*E*)-2-{4-[(*E*)-2-{4-[(*Z*)-2-(4-chlorophenyl)-2-cyanoethenyl]phenyl}ethenyl]-2,5-bis(octyloxy)phenyl}ethenyl]phenyl}-2-propenenitrile (10): Yield 0.84 g (97%); dark red crystals; m.p. 192 °C. − IR (KBr): ṽ = 3010, 2918, 2843, 2208, 1587, 1571, 1502, 1485, 1417, 1245, 1205, 1092, 964, 828. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6 Hz, 6 H, CH_3), 1.25−1.45 (m, 20 H, CH_2), 1.52 (m, 4 H, CH_2), 1.88 (quint, J = 7 Hz, 4 H, β-CH_2), 4.08 (t, J = 6 Hz, 4 H, OCH_2), 7.12 (s, 2 H, 2-H), 7.16 (d, J = 16.4 Hz, 2 H, vin), 7.40 (d, J = 8 Hz, 4 H, 13-H, 16-H), 7.46 (s, 2 H, 10-H), 7.55−7.62 (m, 10 H, CH ar, vin), 7.89 (d, J = 8 Hz, 4 H, CH ar). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.3, 29.3, 29.4, 29.5, 31.8 (CH_2), 69.6 (OCH_2), 109.4 (C-11), 110.7 (C-2), 118.1 (CN), 125.6, 127.9, 132.4, 133.2, 135.1, 140.6, 141.9 (CH,

C_q ar, vin), 127.2, 127.2, 129.3, 129.9 (C-7, C-8, C-13, C-14, C-16, C-17), 151.4 (C-1). − FD MS: *m*/*z* (%) = 860.7 (100) Cl_2 pattern [M^+], 431.5 (16) [M^{2+}]. − $C_{56}H_{58}Cl_2N_2O_2$ (861.977): calcd. C 78.03, H 6.78, N 3.25; found C 78.41, H 6.95, N 3.23.

(2*Z*)-3-[4-{(*E*)-2-[4-{(*E*)-2-[4-{(*Z*)-2-Cyano-2-[4-(trifluoromethyl)-phenyl]ethenyl}phenyl]ethenyl}-2,5-bis(octyloxy)phenyl]-ethenyl}phenyl]-2-[4-(trifluoromethyl)phenyl]-2-propenenitrile (11): Yield 0.89 g (96%); dark red powder; m.p. 187 °C. − IR (KBr): ṽ = 2910, 2845, 2218, 1645, 1575, 1415, 1322, 1205, 1170, 1115, 1070, 962, 845. − ^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6 Hz, 6 H, CH_3), 1.25−1.45 (m, 20 H, CH_2), 1.54 (m, 4 H, CH_2), 1.91(quint, *J* = 7 Hz, 4 H, β-CH_2), 4.08 (t, *J* = 6 Hz, 4 H, OCH_2), 7.12 (s, 2 H, 2-H), 7.17 (d, *J* = 16 Hz, 2 H, vin), 7.55 (s, 2 H, 10-H), 7.61 (d, 2 H, CH vin), 7.67 (d, *J* = 8 Hz, 4 H, 7-H), 7.69−7.79 (AA′BB′ system, 8 H, 13-H, 14-H, 16-H, 17-H), 7.93 (d, *J* = 8 Hz, 4 H, 8-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6, 26.2, 29.2, 29.3, 29.4, 31.7 (CH_2), 69.5 (OCH_2), 109.0 (C-11), 110.8 (C-2), 117.7 (CN), 123.7 (q, $J_{C\text{-}F}$ = 271 Hz, CF_3), 125.1, 125.9, 125.9, 126.0, 127.9, 132.0, 138.1, 140.1, 143.4 (CH, C_q ar, vin), 126.9, 127.9, 130.0 (2 ×, CH ar), 130.8 (q, $J_{C\text{-}F}$ = 33 Hz, C-15), 151.4 (C-1). − FD MS: *m*/*z* (%) = 929.4 (100) [M^+], 464.8 (11) [M^{2+}]. − $C_{58}H_{58}F_6N_2O_2$ (929.084): calcd. C 74.98, H 6.29, N 3.02; found C 74.88, H 6.21, N 3.06.

3-{4-[(*E*)-2-{4-[(*E*)-2-{4-[(*Z*)-2-Cyano-2-(4-methoxyphenyl)-ethenyl]phenyl}ethenyl]-2,5-bis(octyloxy)phenyl}ethenyl]phenyl}-2-(4-methoxyphenyl)-2-propenenitrile (12): Yield 0.72 g (84%); orange solid; m.p. 177 °C. − IR (KBr): ṽ = 3020, 2910, 2840, 2205, 1595, 1503, 1455, 1413, 1242, 1200, 1180, 1030, 965, 825. − ^1H NMR ($CDCl_3$): δ = 0.89 (t, 6 H, CH_3), 1.25−1.63 (m, 20 H, CH_2), 1.90 (quint, *J* = 6.5 Hz, 4 H, β-CH_2), 3.86 (s, 6 H, OCH_3), 4.08 (t, *J* = 6.5 Hz, 4 H, OCH_2), 6.95 (d, *J* = 8.5 Hz, 4 H, 14-H, 16-H), 7.11 (s, 2 H, 2-H), 7.15 (d, *J* = 16 Hz, 2 H, vin), 7.38 (s, 2 H, vin), 7.50−7.64 (m, 10 H), 7.86 (d, *J* = 8 Hz, 4 H, 8-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.3, 29.3, 29.4, 29.5, 31.9 (CH_2), 55.5 (OCH_3), 69.6 (OCH_2), 110.2, 110.7, 114.5 (2 x), 118.4 (CN), 125.2, 126.9 (2 ×), 127.3 (2 ×), 128.0, 129.6 (2 ×), 132.9, 139.6, 139.9(CH, C_q), 151.3, 160.4 (C−O). − FD MS: *m*/*z* (%) = 853.4 (100) [M^+], 427.3 (18) [M^{2+}]. − $C_{58}H_{64}N_2O_4$ (853.140): calcd. C 81.65, H 7.56, N 3.28; found C 81.62, H 7.53, N 3.23.

(2*Z*)-2-[4-{(*Z*)-1-Cyano-2-[4-{(*E*)-2-[4-(hexyloxy)phenyl]-ethenyl}phenyl]ethenyl}-2,5-bis(hexyloxy)phenyl]-3-[4-{(*E*)-2-[4-(hexyloxy)phenyl]ethenyl}phenyl]-2-propenenitrile (13): The synthesis was performed according to the procedure described for **6−12**, using **32**[10] (356 mg, 1 mmol) and **31** (616 mg, 2 mmol). Purification was done by repeated chromatography. Solutions of **13** were protected from light because of photoreactions. Yield: 0.35 g (37%); yellow crystals; m.p. 156 °C. − IR (KBr): ṽ = 3010, 2950, 2915, 2850, 2208, 1585, 1500, 1455, 1410, 1243, 1212, 1170, 1024, 962, 830. − ^1H NMR ($CDCl_3$): δ = 0.88 (m, 12 H, CH_3), 1.22−1.58 (m, 24 H, CH_2), 1.81 (m, 8 H, β-CH_2), 3.97 (t, *J* = 6.5 Hz, 4 H, OCH_2), 4.07 (t, *J* = 6.3 Hz, 4 H, OCH_2), 6.89 (d, *J* = 8.7 Hz, 4 H), 6.97 (d, *J* = 16.8 Hz, 2 H, vin), 7.08 (s, 2 H), 7.15 (d, *J* = 16.8 Hz, 2 H, vin), 7.45 (d, *J* = 8.7 Hz, 4 H), 7.55 (d, *J* = 8.0 Hz, 4 H), 7.67 (s, 2 H, vin), 7.87 (d, *J* = 8.0 Hz, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (2 × CH_3, hex), 22.6, 29.6, 31.6 (2 × CH_2), 25.7, 25.9 (CH_2), 68.1, 69.8 (OCH_2), 107.0, 114.4, 114.8 (CH), 118.3 (CN), 125.4, 125.6, 126.6 (CH), 128.0 (CH), 129.5, 129.8 (CH), 130.3, 132.7, 140.1, 146.2, 150.6 (C−O), 159.4 (C−O). − FD MS: *m*/*z* (%) = 937.3 (100) [M^+], 468.7 (7) [M^{2+}]. − $C_{64}H_{76}N_2O_4$ (937.299): calcd. C 82.01, H 8.17, N 2.99; found C 81.97, H 8.13, N 2.97.

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