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Push-Pull Oligomers with 2,2-Dicyanovinyl Groups as Electron Acceptors

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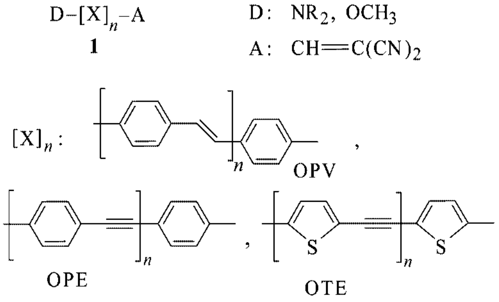
Three conjugated oligomer series with terminal donor–acceptor substitution were studied: oligo(1,4-phenylenevinylene)s DAOPVs **4a**–**d** (n = 1–4), oligo(1,4-phenyleneethynylene)s DAOPEs **6a**–**d** (n = 1–4) and oligo(2,5-thienyleneethynylene)s DAOTEs **8a**–**e** (n = 1–5). Dialkylamino or methoxy groups served as electron donors and 2,2-dicyanovinyl groups as strong electron acceptors. The push-pull effect polarizes the molecular chains – an effect which is documented by the splitting of the ^{13}C chemical shifts of two carbon atoms of the double or triple bonds in the chain. For higher oligomers ($n \geq 3$), the effect is mainly localized at the chain ends. The long-wavelength absorption results in a charge-transfer band which loses gradually its CT character since the intramolecular charge transfer (ICT) declines with increasing numbers n of repeat units (increasing chromophore extension, increasing distance D–A). As a consequence, the DAOPVs **4a**–**d** and the DAOPEs **6a**–**d** represent hypsochromic series, for which the $\lambda_{\max}$ values decrease steadily from $n = 1$ to $n = 4$. This is also true for the DAOTE series **8a**–**e**, but contrary to **4a**–**d** and **6a**–**d** the decrease is very small in the beginning [$\lambda_{\max}(1) - \lambda_{\max}(2)$ = 1 nm] and grows with increasing n to $\lambda_{\max}(4) - \lambda_{\max}(5)$ = 29 nm. Thus, series **8a**–**e** represents an until now unknown type of conjugated push-pull oligomers.

Introduction

Conjugated oligomers and polymers attract much attention because of their interesting properties in materials science.[1] Push-pull systems having terminal donor–acceptor substitution represent a special class of such oligomers.[2]

Their major applications are in the field of nonlinear optics (NLO),[2,3] photorefractive materials (PR)[4] and two-photon absorption (TPA).[5] Normally, conjugated oligomers exhibit a monotonous bathochromic shift of the long-wavelength band when the number n of repeat units is increased. However, a terminal donor–acceptor substitution can change this so that $\lambda_{\max}(n)$ decreases monotonously with increasing numbers n (hypsochromic effect), or is almost constant [$\lambda_{\max}(n) \approx \lambda_{\infty}$], or goes through a maximum for a certain n' before it approaches to λ_{∞}. The specific behavior depends on the strength of donor D and acceptor group A and to a certain extent also on the conjugated chain of the repeat units $[X]_n$ (Scheme 1).[1v,2]

Some time ago we started to study the effect of 2,2-dicyanovinyl groups as very strong electron acceptors in push-pull-substituted conjugated oligomers.[6] Simple series **1** having this acceptor, vinylene or 1,4-phenylene repeat units X and alkoxy or dialkylamino as terminal donor groups are still unknown. We describe here oligomers **1** with composite repeat units, namely oligo(1,4-phenylenevinylene)s (DAOPVs), oligo(1,4-phenyleneethynylene)s (DAOPEs) and oligo(2,5-thienyleneethynylene)s (DAOTEs) bearing 2,2-dicyanovinyl groups as acceptor A and dialkylamino or methoxy groups as donor groups D (Scheme 1).



Scheme 1. Donor–acceptor-substituted conjugated oligomers DAOPVs, DAOPEs and DAOTEs.

Results and Discussion

Synthesis

It turned out that coupling reactions of Sonogashira–Hagihara or Heck type are difficult with 2,2-dicyanovinylbenzene derivatives. Therefore we decided to introduce the desired acceptor group by condensation reactions of the corresponding aldehydes and malononitrile. Scheme 2

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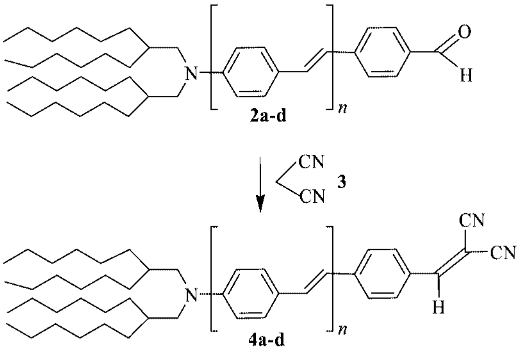
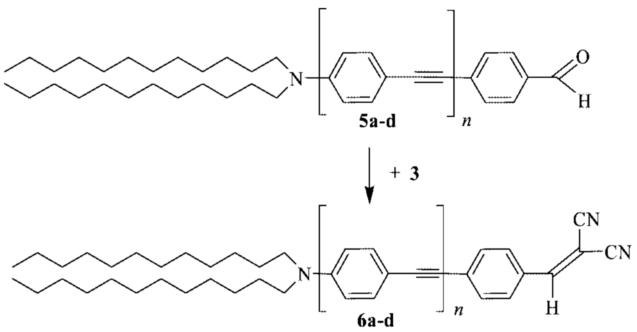
shows the reaction of oligo(1,4-phenylenevinylene)s **2a–d**,[7,8] bearing terminal dialkylamino groups and formyl groups, and malononitrile **3**. The yields of the target compounds **4a–d** are high for the shorter chains and somewhat lower for the longer chains. The branched alkyl chains serve as solubilizing groups. The dicyanovinyl group renders a much lower solubility than the formyl group. Therefore 100 MHz ^{13}C NMR spectra with a reliable signal/noise ratio could only be obtained for **4a–c** but not for **4d**.



4	*n*	Yield [%]	m. p. [°C]
a	1	87	oil
b	2	86	71
c	3	63	167
d	4	69	276

Scheme 2. Preparation of the DAOPVs **4a–d**.

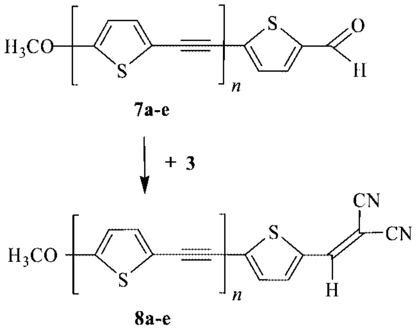
Scheme 3 shows the related procedure for the preparation of the DAOPEs **6a–d**. The aldehydes **5a–d**[9] and malononitrile (**3**) react to the target compounds **6a–d**. The yields are very high for the first members of the series and decrease with increasing chain length. The didodecylamino group serves as donor group and enhances the solubility. Analogous to **4d**, a ^{13}C NMR spectrum of **6d** could not be obtained. Since **6d** is even less soluble in $CDCl_3$ than **4d**, the ^{1}H NMR spectrum of **6d** was measured in $CDCl_2$–$CDCl_2$ at 60 °C.



6	*n*	Yield [%]	m. p. [°C]
a	1	98	46
b	2	94	89
c	3	88	178
d	4	54	>250

Scheme 3. Preparation of the DAOPEs **6a–d**.

Scheme 4 demonstrates the preparation of the DAOTEs **8a–e**. The aldehydes **7a–e**[10] react with **3** to generate the target compounds **8a–e**. The yields are again high for the lower members of the series and decrease with increasing chain length. The solubilizing properties of the methoxy group are comparably low, but the OTE chain provides a better solubility than the OPV and OPE chains. Therefore ^{1}H NMR spectra of **8a–e** and ^{13}C NMR spectra of **8a–d** could be obtained in $CDCl_3$.



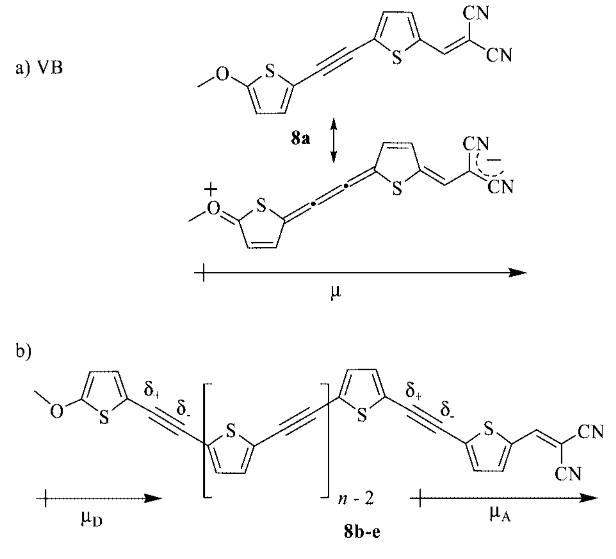
8	*n*	Yield [%]	m. p. [°C]
a	1	93	133
b	2	94	155
c	3	89	167
d	4	62	174
e	5	38	182

Scheme 4. Preparation of the OTEs **8a–e** having terminal donor–acceptor substitution.

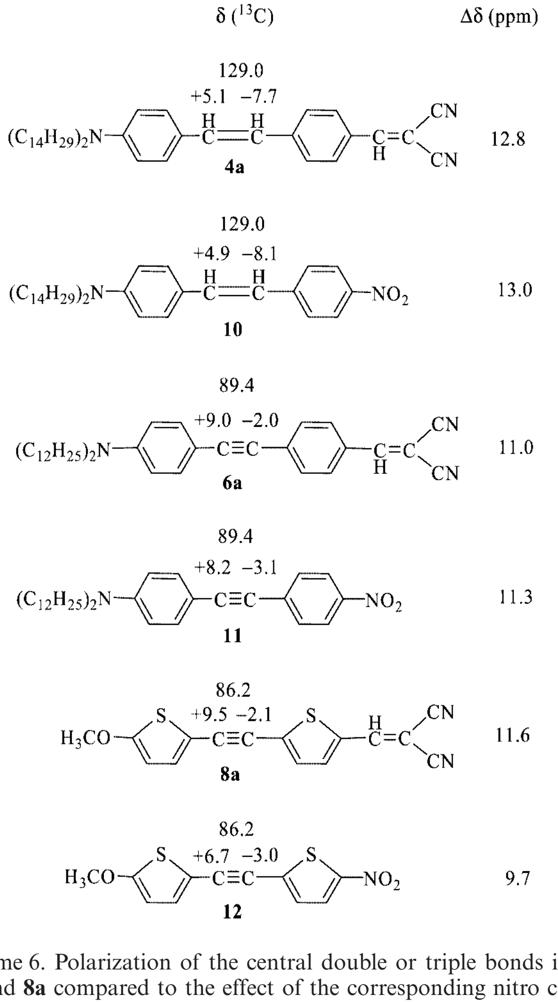
Push-Pull Effect

The push-pull effect of the DAOVPs **4a–4d**, DAOPEs **6a–6d** and DAOTEs **8a–8e** provokes a polarization of the molecules in the ground state S_0. This can be expressed by the participation of dipolar resonance structures (valence bond theory VB) or – in particular for the higher members ($n \geq 2$) of the series – better by dipolar segments having partial dipole moments μ_D and μ_A at the chain ends.[7,9] Scheme 5 demonstrates the two models for series **8**.

The double bonds in **4a** and the triple bonds in **6a** and **8a** are strongly polarized. Scheme 6 demonstrates this in comparison to the corresponding systems **10**,[7] **11**[9] and **12**[10] which bear NO_2 groups instead of dicyanovinyl groups. ^{13}C Chemical shifts are very sensitive toward changes in the electron density. The donor groups cause a high-field shift and the acceptor group a low-field shift – each in the β-position of the multiple bonds. Thus, the olefinic carbon atoms in **4a** have the δ values 129.0 + 5.1 = 134.1 and 129.0 – 7.2 = 121.8 ppm (Scheme 6); δ = 129.0 ppm is the ^{13}C chemical shift for the unsubstituted (*E*)-stilbene, 89.4 for tolane and 86.2 for dithienylacetylene. The $\Delta\delta$ values of the olefinic or acetylenic carbon atoms listed in Scheme 6 indicate the polarization of the multiple bonds. AM1 calculations of OPVs. and OPEs with the DA combination $N(CH_3)_2/NO_2$ revealed that the $\Delta\delta$ values ob-



Scheme 5. Visualization of the push-pull effect of the DAOTEs **8**: a) VB model of **8a**, b) model with terminal partial dipole moments μ_A and μ_D for **8b**–**e**.



Scheme 6. Polarization of the central double or triple bonds in **4**, **6a** and **8a** compared to the effect of the corresponding nitro compounds **10**, **11** and **12** (*δ* values: ^{13}C chemical shifts in CDCl$_3$ related to TMS as internal standard, Δ*δ*: shift differences of the multiple bonds).

tained for the double or triple bonds correlate exactly with the charge differences Δ*q* for these bonds.[7,9] The effect of the dicyanovinyl group is similar (**4a/10**, **6a/11**) or even stronger (**8a/12**) than the effect of the nitro group.

Extension of the chains **4**, **6** and **8** leads in all cases to a decrease of the Δ*δ* values with increasing numbers *n*. The measured *δ* values for the terminal multiple bonds and their differences Δ*δ* are listed in Table 1. The Δ*δ* values for example in series **8a**–**d** decline from 11.6 to 5.1 and 5.2, respectively. The latter values are typical for purely donor or purely acceptor-substituted compounds;[7–10] that means the push-pull effect disappears completely with increasing distance A–D.

Table 1. ^{13}C NMR spectroscopic data of the terminal double/triple bonds (*δ* values in CDCl$_3$ related to TMS as internal standard, Δ*δ* values indicating the polarization of the multiple bonds).

		Donor side — C≡C —			Acceptor side — C≡C —		
	n	*δ*(α)	*δ*(β)	Δ*δ*	*δ*(α)	*δ*(β)	Δ*δ*
4a	1	134.1	121.3	12.8	121.3	134.1	12.8
4b	2	129.9	122.7	7.2	125.7	133.1	7.4
4c	3	129.2	123.0	6.2	127.0	133.0	6.0
6a	1	98.4	87.4	11.0	87.4	98.4	11.0
6b	2	94.0	86.9	7.1	89.7	95.2	5.5
6c	3	93.4	87.0	6.4	90.1	94.7	4.6
8a	1	95.7	84.1	11.6	84.1	95.7	11.6
8b	2	89.7	83.5	6.2	86.4	92.0	5.6
8c	3	88.9	83.6	5.3	88.4	93.4	5.0
8d	4	88.7	83.6	5.1	88.2	93.4	5.2

The inner multiple bonds in **4c**, **6c**, **8c** and **8d** do not exhibit a significant polarization (Δ*δ* < 1.0). This result is in accordance with the second model in Scheme 5. A DFT//B3LYP/6-31G* study of a compound related to **8b**, which contains a 4-dimethylaminophenyl group instead of a 5-methoxythien-2-yl group came to the corresponding result, that the polarization induced by the push-pull effect is mainly present in the chain ends but not in the center.[11]

UV/Vis Absorption

The long-wavelength electron transition of conjugated systems is strongly influenced by push-pull effects. There are several possibilities to estimate the strength of the push-pull effect of terminal donor and acceptor groups on a conjugated chain.[12] A simple method consists of the energy difference Δ*E* between the frontier HOMO (donor) and LUMO (acceptor) in isolated individual molecules. The smaller the |Δ*E*| value is, the stronger is the push-pull effect.[12a] Dimethylaminobenzene and nitrobenzene give for example a |Δ*E*| value of 7.42 eV for DAOPV or DAOPE series with terminal dimethylamino and nitro groups.[12a] Since 2-cyanocinnamonitrile is a stronger acceptor compound than nitrobenzene, the |Δ*E*| value for the series **4a**–**d** and **6a**–**d** should be even lower. More accurate methods take the individual π-chain with its coupling to the frontier orbitals of D and A into account. In particular this seems to be necessary for the OTE series **8a**–**e**. According to earlier findings,[2] the intramolecular charge transfer (ICT), which is involved in the long-wavelength absorption, is better fulfilled for 2,5-thienylenevinylene repeat units than for 1,4-phenylenevinylene or 1,4-phenyleneethynylene units.

The long-wavelength absorption maxima of three series **4a**–**d** and **6a**–**d** and **8**–**e** are visualized in Figure 1. The DAOPVs **4a**–**d** and the DAOPEs **6a**–**d** are hypsochromic series; that means extension of the chromophore (increasing values *n*) leads to continous blue-shifts of the absorption bands. The strong push-pull effect of the D/A-combination R_2N/$CH{=}C(CN)_2$ or CH_3O/$CH{=}C(CN)_2$ causes a strong ICT for the lowest members **4a**, **6a** and **8a** ($n = 1$) of the three series, where the distances D–A are small. Increasing values *n* provoke a decreasing ICT. The red-shift caused by ICT is then diminished. This leads to an overall hypsochromic effect because the extension of the chromophores can not compensate the influence of the decreasing ICT on the long-wavelength absorption. The charge-transfer band loses gradually its CT character.[2] Both series **4** and **6** should approach to limiting values λ_∞, whose prediction[2] would demand the comparison with the corresponding series without push-pull effect, which is unknown.

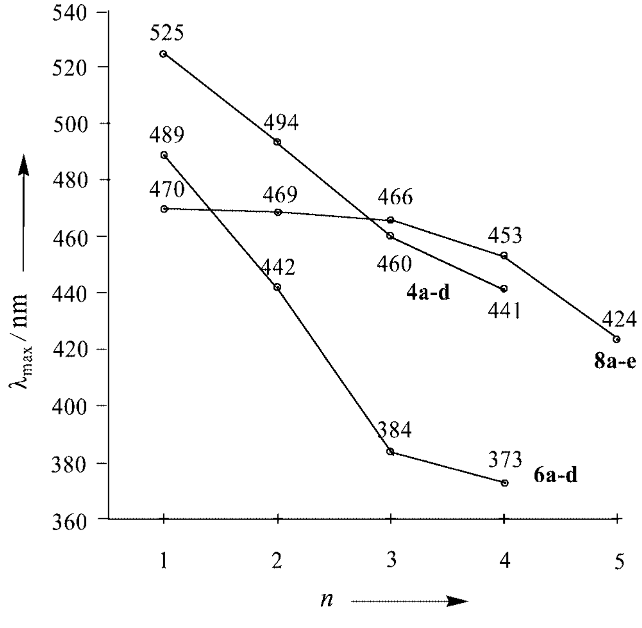


Figure 1. Long-wavelength absorption maxima of the OPVs **4a**–**d** (n = 1–4), OPEs **6a**–**d** (n = 1–4) and OTEs **8a**–**e** (n = 1–5) (measurements in $CDCl_3$).[13]

Whereas the differences [$\lambda_{max}(n) - \lambda_{max}(n+1)$] decrease with increasing numbers *n* for the two series DAOPV (**4a**–**d**) and DAOPE (**6a**–**d**), the OTE series **8a**–**e** behaves opposite in the measured range n = 1–5. The absorption maxima for **8a** ($n = 1$) and **8b** ($n = 2$) are almost equal; that means the extension of the chromophore from $n = 1$ to $n = 2$ can nearly compensate the decrease of the ICT in the mutual influence on the electron transition energy. Nevertheless, series **8** must approach to a limiting value λ_∞, too.[2] We interpret the behavior of **8** in that way, that this series belongs to a special type of push-pull-substituted conjugated oligomers, in which the transition ergies $\Delta E(n)$ pass through a minimum for a certain n' and then enter for higher *n* values into a region of convergence to λ_∞.[2] In series **8**, this minimum is already reached for $n = 1$, but the region of convergence is characterized by a high effective conjugation length n_{ECL}. For the unsubstituted OTE series an n_{ECL} value of 12 was estimated.[14] Certainly many more (than five) members of series **8** have to be studied in order to see the convergence region and the approach to λ_∞.

Conclusions

Conjugated oligomers **4a**–**d**, **6a**–**d** and **8a**–**e**, having 1,4-phenylenevinylene, 1,4-phenyleneethynylene or 2,5-thienyleneethynylene repeat units [n = 1–4,(5)] and terminal donor–acceptor substitution [R_2N/$CH{=}C(CN)_2$ or CH_3O/$CH{=}C(CN)_2$] were obtained by Knoevenagel condensation reactions of the corresponding aldehydes and malononitrile. The push-pull effect of the compounds leads to a polarization of the chains, for $n > 2$ in particular of the chain ends. An MO oriented model takes this better into account than a VB model. An easy experimental proof of the polarization is possible on the basis of the ^{13}C chemical shift differences $\Delta\delta$ of the two carbon atoms of each double or triple bond in the chain.

The intramolecular charge transfer (ICT) plays an outstanding role for the long-wavelength absorption. It causes, induced by the change of the electron correlation energy[2] a red-shift which decreases with increasing numbers *n* of repeat units, that means with increasing distance D–A. The charge-transfer band loses gradually its character. Since the extension of the conjugation can not compensate this effect, all three discussed oligomer series are hypsochromic series. Whereas the DAOPVs **4a**–**d** and the DAOPEs **6a**–**d** exhibit this behavior in a mode reminiscent of some other recently found[7–9] push-pull oligomers, the series DAOTE **8a**–**e** belongs to a new type. Within the studied region of n = 1–5, the λ_{max} values are first almost constant and decrease then more and more. Obviously, the extension of the conjugation can nearly compensate the decrease of the ICT only up to $n = 3$.

Experimental Section

General: The melting points were measured with a Büchi melting point apparatus and are uncorrected. The UV/Vis spectra were obtained with a Zeiss MCS 320/340 spectrometer. The ^1H and ^{13}C NMR spectra were recorded with the Bruker spectrometer AMX 400. $CDCl_3$ served as solvent unless otherwise noted, and TMS was used as the internal standard.

The field desorption (FD) mass spectra were obtained with a Finnigan MAT 95 and the ESI (electrospray ionisation) mass spectra with a Micromass/Waters QTOF Ultima 3 spectrometer. Elemental analyses were performed in the microanalytical laboratory of the Institute of Organic Chemistry of the University of Mainz.

General Procedure for the Knoevenagel Condensation Reaction of Aldehydes 2, 5, 7 and Malononitrile (3): A concentrated solution of aldehyde **2a–d**, **5a–d or 7a–d** (1.0–1.5 mmol) and 1.1 equiv. (1.1–1.55 mmol) malononitrile (**3**) in 15–300 mL CH_2Cl_2 was stirred at room temperature in the presence of 85–130 mg (1.0–1.5 mmol) piperidine. TLC control (SiO_2, CH_2Cl_2) showed the progress of the reaction. For the higher members of the series (n = 3–5) refluxing of the solution was necessary to bring the reaction to the end (when TLC indicated the total consumption of the aldehyde). The volatile parts were evaporated and the residue purified by column chromatography [(5×40 cm SiO_2), petroleum, b.p. 40–70 °C/CH_2Cl_2, 1:1] and/or recrystallization from CH_2Cl_2, to which petroleum (b.p. 40–70 °C) was added in the heat till the solution became turbid. (Only **4a** is a viscous oil, which did not crystallize).

2-[4-((*E*)-2-{4-[Bis(2-hexyloctyl)amino]phenyl}ethenyl)benzylidene]-malononitrile (4a): Yield 578 mg, 87%,[15,16] red oil. ^1H NMR ($CDCl_3$): δ = 0.87 (t, 12 H, CH_3), 1.24 (m, 40 H, CH_2), 1.83 (m, 2 H, CH), 3.23 (d, 4 H, NCH_2), 6.63/7.36 (AA′MM′, 4 H, aromat. H, donor side), 6.86/7.22 (AB, ^3J = 16.1 Hz, 2 H, olefin. H), 7.54/7.84 (AA′BB′, 4 H, aromat. H, acceptor side), 7.63 [s, 1 H, $CH=C(CN)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.4, 29.8, 31.6, 31.9 (CH_2), 35.6 (CH), 56.7 (CH_2N), 79.3, 158.7 [$CH=C(CN)_2$], 112.5, 126.5, 128.6, 131.6 (aromat. CH), 113.4, 114.5 (CN), 121.3, 134.1 (olefin. CH), 123.1, 128.7, 145.5, 149.0 (aromat. C_q) ppm. FD MS: m/z (%) = 664 (100) [M^+]. UV/Vis ($CHCl_3$): λ_{max} = 525 nm ($\log\varepsilon$ = 4.50). $C_{46}H_{69}N_3$ (664.1): calcd. C 83.20, H 10.47, N 6.33; found C 83.54, H 10.38, N 6.22.

2-(4-{(*E*)-2-[4-((*E*)-2-{4-[Bis(2-hexyloctyl)amino]phenyl}ethenyl)-phenyl]ethenyl}benzylidene)malononitrile (4b): Yield 659 mg, 86%, red crystals, m.p. 71 °C. ^1H NMR ($CDCl_3$): δ = 0.87 (t, 12 H, CH_3), 1.25 (m, 40 H, CH_2), 1.83 (m, 2 H, CH), 3.22 (d, 4 H, NCH_2), 6.63/7.36 (AA′MM′, 4 H, aromat. H, donor side), 6.86/7.07 (AB, ^3J = 16.2 Hz, 2 H, olefin. H, donor side), 7.07/7.27 (AB, ^3J = 16.2 Hz, 2 H, olefin. H, acceptor side), 7.46/7.50 (AA′BB′, 4 H, aromat. H), 7.61/7.88 (AA′BB′, 4 H, aromat. H, acceptor side), 7.67 [s, 1 H, $CH=C(CN)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.4, 29.8, 31.9 (CH_2), 35.6 (CH), 56.7 (CH_2N), 80.7, 158.7 [$CH=C(CN)_2$], 112.6, 126.3, 127.2, 127.5, 127.7, 131.5 (aromat. CH), 113.1, 114.2 (CN), 122.7, 125.7, 129.9, 133.3 (olefin. CH), 124.0, 129.7, 134.3, 139.3, 144.2, 148.3 (aromat. C_q) ppm. FD MS: m/z (%) = 767 (100) [M + H^+]. UV/Vis ($CHCl_3$): λ_{max} = 494 nm ($\log\varepsilon$ = 4.65). $C_{54}H_{75}N_3$ (766.2): calcd. C 84.65, H 9.87, N 5.48; found C 84.20, H 9.94, N 5.36.

2-{4-[(*E*)-2-(4-{(*E*)-2-[4-((*E*)-2-{4-[Bis(2-hexyloctyl)amino]-phenyl}ethenyl)phenyl]ethenyl}phenyl)ethenyl]benzylidene}-malononitrile (4c): Yield 547 mg, 63%, red crystals, m.p. 167 °C. ^1H NMR ($CDCl_3$): δ = 0.88 (t, 12 H, CH_3), 1.25 (m, 40 H, CH_2), 1.84 (m, 2 H, CH), 3.22 (d, 4 H, NCH_2), 6.63/7.36 (AA′MM′, 4 H, Ar-H, donor side), 6.86/7.04 (AB, ^3J = 16.0 Hz, 2 H, olefin. H, donor side), 7.06/7.13 (AB, ^3J = 16.4 Hz, 2 H, olefin. H), 7.09/7.26 (AB, ^3J = 16.4 Hz, 2 H, olefin. H, acceptor side), 7.43/7.47 (AA′BB′, 4 H, aromat. H), 7.51 ("s", 4 H, aromat. H), 7.60/7.88 (AA′BB′, 4 H, aromat. H, acceptor side), 7.65 [s, 1 H, $CH=C(CN)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.6, 26.3, 29.8, 31.6, 31.9 (CH_2), 35.6 (CH), 56.7 (NCH_2), 80.9, 158.7 [$CH=C(CN)_2$], 112.7, 126.2, 126.9, 127.2, 127.5, 127.6, 129.3, 131.5 (aromat. CH), 113.0, 114.1 (CN), 123.0, 126.3, 126.9, 127.0, 129.2, 133.0 (olefin. CH), 124.2, 129.8, 135.2, 135.3, 138.2, 138.3, 143.9, 148.2 (aromat. C_q) ppm. FD MS: m/z (%) = 869 (100) [M + H^+]. UV/Vis ($CHCl_3$): λ_{max} = 460 nm ($\log\varepsilon$ = 4.88). $C_{62}H_{81}N_3$ (868.4): calcd. C 85.76, H 9.40, N 4.84; found C 85.80, H 9.51, N 4.63.

2-[4-((*E*)-2-{4-[(*E*)-2-(4-{(*E*)-2-[4-((*E*)-2-{4-[Bis(2-hexyloctyl)-amino]phenyl}ethenyl)phenyl]ethenyl}phenyl)ethenyl]phenyl}ethenyl)-benzylidene]malononitrile (4d): Yield 670 mg, 69%, red crystals, m.p. 276 °C. ^1H NMR ($CDCl_3$): δ = 0.87 (t, 12 H, CH_3), 1.24 (m, 40 H, CH_2), 1.83 (m, 2 H, CH), 3.21 (d, 4 H, NCH_2), 6.62/7.35 (AA′MM′, 4 H, aromat. H, donor side), 6.86/7.04 (AB, ^3J = 16.0 Hz, 2 H, olefin. H, donor side), 7.08–7.14 (m, 5 H, olefin. H), 7.28 (d, ^3J = 16.1 Hz, 1 H, olefin. H, acceptor side), 7.43/7.47 (AA′BB′, 4 H, aromat. H), 7.50 ("s", 4 H, aromat. H), 7.53 ("s", 4 H, aromat. H), 7.62/7.89 (AA′BB′, 4 H, aromat. H, acceptor side), 7.68 [s, 1 H, $CH=C(CN)_2$] ppm. FD MS: m/z (%) = 971 (100) [M + H^+]. UV/Vis ($CHCl_3$): λ_{max} = 441 nnm ($\log\varepsilon \approx$ 5.0). $C_{70}H_{87}N_3$ (970.5): calcd. C 86.63, H 9.04, N 4.33; found C 86.36, H 9.23, N 4.11.

2-{4-[4-(Didodecylamino)phenylethynyl]benzylidene}malononitrile (6a): Yield 593 mg, 98%, dark red crystals, m.p. 46 °C. ^1H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.26 (t, 4 H, NCH_2), 6.56/7.36 (AA′MM′, 4 H, aromat. H, donor side), 7.54/7.84 (AA′BB′, 4 H, aromat. H, acceptor side), 7.67 (s, 1 H, olefin. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.6, 27.1, 27.2, 29.1, 29.3, 29.5, 29.6, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 81.3, 158.6 [$CH=C(CN)_2$], 87.4, 98.4 (alkyne C), 107.2, 129.1, 131.5, 148.7 (aromat. C_q), 111.2, 130.7, 131.7, 133.5 (aromat. CH), 112.9, 114.0 (CN) ppm. FD MS: m/z (%) = 606 (100) [M + H^+]. UV/Vis ($CHCl_3$): λ_{max} = 489 nm ($\log\varepsilon$ = 4.45). $C_{42}H_{59}N_3$ (606.0): calcd. C 83.25, H 9.81, N 6.93; found C 83.37, H 9.82, N 6.85.

2-(4-{4-[4-(Didodecylamino)phenylethynyl]phenylethynyl}-benzylidene)malononitrile (6b): Yield 664 mg, 94%, red crystals, m.p. 89 °C. ^1H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.25 (m, 36 H, CH_2), 1.53 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.54/7.34 (AA′MM′, 4 H, aromat. H, donor side), 7.47 ("s", 4 H, aromat. H), 7.62/7.87 (AA′BB′, 4 H, aromat. H, acceptor side), 7.71 (s, 1 H, olefin. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.6, 27.1, 27.2, 29.3, 29.5, 29.6, 31.7 (CH_2, partly superimposed), 50.9 (NCH_2), 82.6, 158.4 [$CH=C(CN)_2$], 86.9, 89.7, 94.0, 95.2 (alkyne C), 108.1, 120.6, 125.5, 130.2, 131.1, 148.2 (aromat. C_q), 111.2, 130.6, 131.2, 132.4, 132.9, 137.7 (aromat. CH), 112.6, 113.7 (CN) ppm. FD MS: m/z (%) = 706 (100) [M + H^+]. UV/Vis ($CHCl_3$): λ_{max} = 442 nm ($\log\varepsilon$ = 4.56). $C_{50}H_{63}N_3$ (706.1): calcd. C 85.06, H 8.99, N 5.95; found C 85.02, H 8.94, N 5.74.

2-[4-(4-{4-[4-(Didodecylamino)phenylethynyl]phenylethynyl}-phenylethynyl)benzylidene]malononitrile (6c): Yield 709 mg, 88%, red crystals, m.p. 178 °C. ^1H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.53 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.55/7.34 (AA′MM′, 4 H, aromat. H, donor side), 7.45 ("s", 4 H, aromat. H), 7.51 ("s", 4 H, aromat. H), 7.64/7.88 (AA′BB′, 4 H, aromat. H, acceptor side), 7.72 (s, 1 H, olefin. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.6, 27.1, 27.2, 29.3, 29.4, 29.5, 29.6, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 82.8, 158.4 [$CH=C(CN)_2$], 86.9, 88.5, 90.1, 90.2, 93.4, 94.7 (alkyne C), 108.2, 121.8, 124.2, 124.2, 124.5, 130.3, 131.5, 148.2 (aromat. C_q), 111.1, 130.6, 131.1, 131.4, 131.6, 131.8, 132.4, 132.9 (aromat. CH), 112.5, 113.6 (CN) ppm. FD MS: m/z (%) = 806 (100) [M + H^+]. UV/Vis ($CHCl_3$): λ_{max} = 384 nm ($\log\varepsilon$ = 4.75). $C_{58}H_{67}N_3$ (806.2): calcd. C 86.41, H 8.38, N 5.21; found C 86.62, H 8.51, N 5.23.

2-{4-[4-(4-{4-[4-(Didodecylamino)phenylethynyl]phenylethynyl}-phenylethynyl)phenylethynyl]benzylidene}malononitrile (6d): Yield 489 mg, 54%, red crystals, m.p. >250 °C (recrystallization from CH_2Cl_2/CH_3OH, 2:1). ^1H NMR ($CDCl_2$-$CDCl_2$, 60 °C.): δ = 0.86 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.53 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.55/7.35 (AA′MM′, 4 H, aromat. H, donor side), 7.42–7.53 (m, 12 H, aromat. H), 7.65/7.89 (AA′BB′, 4 H, aromat. H, acceptor side), 7.73 (s, 1 H, olefin. H) ppm. FD MS: m/z (%) = 907 (100) [M + H^+]. UV/Vis ($CHCl_3$): λ_{max} = 373 nm ($\log\varepsilon$ = 4.94).

HRMS (ESI): calcd. for [$C_{66}H_{71}N_3$ + H^+] 906.5696; found: 906.5708.

2-[5-(5-Methoxythiophen-2-ylethynyl)thiophen-2-ylmethylene]-malononitrile (8a): Yield 275 mg, 93%, red crystals, m.p. 133 °C. ^{1}H NMR ($CDCl_3$): δ = 3.92 (s, 3 H, OCH_3), 6.15/7.04 (AX, ^3J = 4.1 Hz, 2 H, thienylene, donor side), 7.22/7.60 (AX, ^3J = 3.5 Hz, 2 H, thienylene, acceptor side), 7.71 (s, 1 H, olefin. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 60.4 (OCH_3), 77.4, 149.7 [CH=C(CN)$_2$], 84.1, 95.7 (alkyne C), 104.9, 131.7, 133.3, 138.5 (CH), 107.3, 135.1, 135.2, 167.4 (C_q), 113.2, 113.9 (CN) ppm. FD MS: m/z (%) = 296 (100) [$M^{+\cdot}$]. UV/Vis ($CHCl_3$): λ_{max} = 470 nm (logε = 4.53). $C_{15}H_8N_2OS_2$ (296.0): calcd. C 60.79, H 2.72, N 9.45, S 21.64; found C 60.65, H 2.51, N 9.71, S 21.48.

2-{5-[5-(5-Methoxythiophen-2-ylethynyl)thiophen-2-ylethynyl]-thiophen-2-ylmethylene}malononitrile (8b): Yield 378 mg, 94%, red-brown crystals, m.p. 155 °C. ^{1}H NMR ($CDCl_3$): δ = 3.92 (OCH_3), 6.12/6.97 (AX, ^3J = 4.1 Hz, 2 H, thienylene, donor side), 7.11/7.21 (AB, ^3J = 4.0 Hz, 2 H, thienylene), 7.31/7.64 (AX, ^3J = 4.1 Hz, 2 H, thienylene, acceptor side), 7.71 (s, 1 H, olefin. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 60.3 (OCH_3), 78.3, 149.7 [CH=C(CN)$_2$], 83.4, 86.4, 89.7, 92.0 (alkyne C), 104.4, 131.6, 131.9, 132.6, 133.7, 138.4 (CH), 108.4, 121.9, 126.5, 135.6, 135.8, 168.2 (C_q), 113.0, 113.1 (CN) ppm. FD MS: m/z (%) = 403 (100) [M + H^+]. UV/Vis ($CHCl_3$): λ_{max} = 469 nm (logε = 4.60). $C_{21}H_{10}N_2OS_3$ (402.5): calcd. C 62.67, H 2.50, N 6.96, S 23.90; found C 62.53, H 2.79, N 6.73, S 23.63.

2-(5-{5-[5-(5-Methoxythiophen-2-ylethynyl)thiophen-2-ylethynyl]-thiophen-2-ylethynyl} thiophen-2-ylmethylene)malononitrile (8c): Yield 453 mg, 89%, red crystals, m.p. 167 °C. ^{1}H NMR ($CDCl_3$): δ = 3.89 (s, 3 H, OCH_3), 6.10/6.96 (AX, ^3J = 4.1 Hz, 2 H, thienylene, donor side), 7.08/7.15 (AB, ^3J = 4.0 Hz, 2 H, thienylene), 7.17/7.24 (AB, ^3J = 4.0 Hz, 2 H, thienylene), 7.32/7.64 (AB, ^3J = 4.1 Hz, 2 H, thienylene, acceptor side), 7.75 (s, 2 H, olefin. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 60.3 (OCH_3), 78.4, 149.7 [CH=C(CN)$_2$], 83.6, 86.4, 86.6, 88.4, 88.9, 93.4 (alkyne C), 104.3, 131.6, 131.7, 132.4, 132.7, 132.8, 133.7, 138.3 (CH), 108.4, 122.8, 123.1, 125.9, 126.4, 135.8, 136.0, 168.2 (C_q), 113.0, 113.7 (CN) ppm. FD MS: m/z (%) = 509 (100) [M + H^+]. UV/Vis ($CHCl_3$): λ_{max} = 466 nm (logε = 4.65). $C_{27}H_{12}N_2OS_4$ (508.7): calcd. C 63.76, H 2.38, N 5.51, S 25.21; found C 63.47, H 2.14, N 5.59, S 25.09.

2-[5-(5-{5-[5-(5-Methoxythiophen-2-ylethynyl)thiophen-2-ylethynyl]-thiophen-2-ylethynyl}thiophen-2-ylethynyl)thiophen-2-ylmethylene]-malononitrile (8d): Yield 381 mg, 62%, red crystals, m.p. 174 °C. ^{1}H NMR ($CDCl_3$): δ = 3.89 (s, 3 H, OCH_3), 6.09/6.96 (AX, ^3J = 4.1 Hz, 2 H, thienylene, donor side), 7.08/7.14 (AB, ^3J = 4.0 Hz, 1 H, thienylene), 7.16–7.25 (m, 4 H, thienylene), 7.32/7.64 (AX, ^3J = 4.2 Hz, 2 H, thienylene, acceptor side), 7.74 (s, 1 H, olefin. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 60.3 (OCH_3), 78.8, 149.7 [CH=C(CN)$_2$], 83.6, 86.6, 86.7, 86.8, 87.6, 88.2, 88.7, 93.4 (alkyne C), 104.3, 131.6, 131.7, 132.3, 132.4, 132.5, 132.7, 132.8, 133.7, 138.3 (CH), 108.4, 122.3, 123.3, 123.9, 125.0, 125.6, 126.2, 136.0, 136.0, 168.2 (C_q), 113.0, 113.7 (CN) ppm. FD MS: m/z (%) = 615 (100) [M + H^+]. UV/Vis ($CHCl_3$): λ_{max} = 453 nm (logε = 4.72). $C_{33}H_{14}N_2OS_5$ (614.0): calcd. C 64.47, H 2.30, N 4.56, S 26.07; found C 64.66, H 2.46, N 4.51, S 25.98.

2-{5-[5-(5-{5-[5-(5-Methoxythiophen-2-ylethynyl)thiophen-2-ylethynyl]thiophen-2-ylethynyl}thiophen-2-ylethynyl)thiophen-2-ylethynyl]-thiophen-2-ylmethylene}malononitrile (8e): Yield 274 mg, 38%, red crystals, m.p. 182 °C. ^{1}H NMR ($CDCl_3$): δ = 3.89 (s, 3 H, OCH_3), 6.09/6.95 (AX, ^3J = 4.1 Hz, 2 H, thienylene, donor side), 7.08/7.14 (AB, ^3J = 4.0 Hz, 2 H, thienylene), 7.16–7.25 (m, 6 H, thienylene), 7.32/7.64 (AX, ^3J = 4.2 Hz, 2 H, thienylene, acceptor side), 7.74 (s, 1 H, olefin. H) ppm. FD MS: m/z (%) = 721 (100) [M + H^+]. UV/Vis ($CHCl_3$): λ_{max} = 424 nm (logε = 4.85). $C_{39}H_{16}N_2OS_6$ (720.9): calcd. C 64.98, H 2.24, N 3.89, S 26.68; found C 64.82, H 2.28, N 3.92, S 26.79.

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