Methylium Ions with OPV Chains − New NIR Dyes

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Carbinols, which contain three OPV chains, were generated in convergent syntheses. The extension of the conjugation leads to a bathochromic effect that shifts the absorption from the UV into the visible region. The carbinol series has a convergence limit of the absorption at λ_{max} = 415 nm. The corresponding carbenium ions exhibit a stronger bathochromic shift with the increasing number of repeating units in each chain. Thus, NIR dyes were obtained which show a convergence limit at λ_{max} = 879 nm. The charge distribution in the ground state of the carbocations is discussed on the basis of ^{13}C NMR spectroscopic data.

Introduction

Conjugated oligomers like oligo(1,4-phenylenevinylene)s (OPV) attract a lot of attention because they serve as monodisperse model compounds for polymers. Moreover, their own electric, optical and optoelectronic properties promise interesting applications in materials science.[1−6] Triphenylmethylium ions, on the other hand, play an outstanding role among the carbenium ions because they represent the structural framework for triphenylmethane dyes. The objective of our work was to combine these two structural principles and generate methylium ions with three OPV chains. The increasing length of the conjugated chains should provoke a strong bathochromic shift of the absorption. Thus, NIR dyes should be obtained.

Results and Discussion

In order to avoid structural defects, we conceived a convergent synthesis in which the preformed, constitutionally and configurationally pure chains were fixed to the core in the final step. Tritolylmethane (**1**) was transformed into the threefold phosphonate **2** which served as building block for the core. The "arms" were generated by Wittig−Horner reactions of 3,4,5-trihexyloxybenzaldehyde (**3a**) and the monophophonate **4**. Since **4** contains a protected formyl group, acidic workup yielded an aldehyde **3b**, which could be applied again in the reaction with the phosphonate **4**. Thus, a series of aldehydes **3a**−**d** with extended conjugation could be obtained.[7] The purified all-*trans* configured aldehydes were used for the preparation of the carbinols **5a**−**d**. Remarkably, in the presence of air no further oxidant was necessary for the formation of **5a**−**d**.

Protonation of **5a**−**d** in chloroform/trifluoroacetic acid (7:3) led to the quantitative formation of the methylium ions **6a**−**d**. The isolation of the salts as tetrafluoroborates is best performed by protonation with HBF_4 and precipitation from acetic anhydride. The dark blue-green solids decompose on heating above 230 °C. In wet solvents hydrolysis leads back to the carbinols **5a**−**d**.

The hexyloxy chains strongly enhance the solubility. The generation of the unsubstituted OPV systems **5** and **6** proved to be impossible; even the tristilbenyl system[8] is hardly soluble. Additionally, the hexyloxy substituents cause a push-pull character of the methylium ions. Figure 1 shows the UV/Vis/NIR spectra of the carbinol **5c** and the corresponding cation **6c**.

The dependence of the long wavelength absorptions of **5a**−**d** and **6a**−**d** on the number *n* of repeating units is demonstrated in Figure 2. Both series exhibit a monotonous growth of λ_{max} with increasing *n*. The convergence $\lambda_{max} \rightarrow \lambda_{\infty}$ ($n \rightarrow \infty$) of conjugated oligomers can be determined by

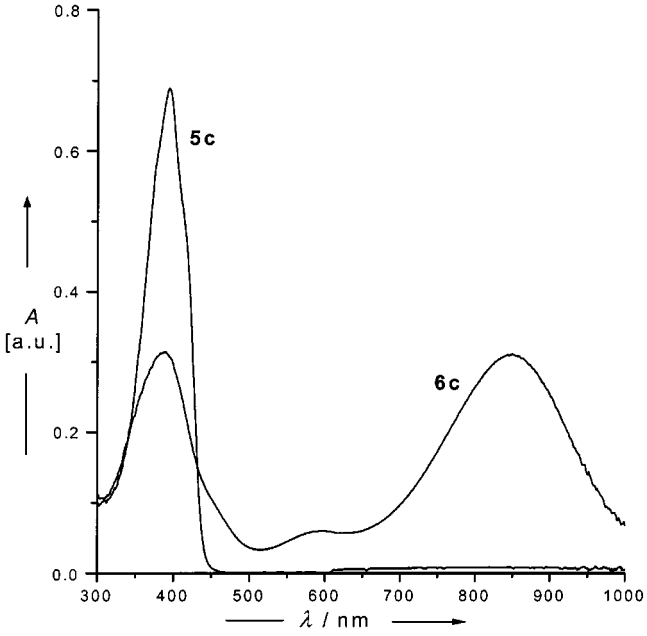

Figure 1. UV/Vis/NIR spectra of the carbinol **5c** (measured in $CHCl_3$) and the corresponding trifluoroacetate **6c** (measured in $CHCl_3/CF_3COOH$, 7:3)

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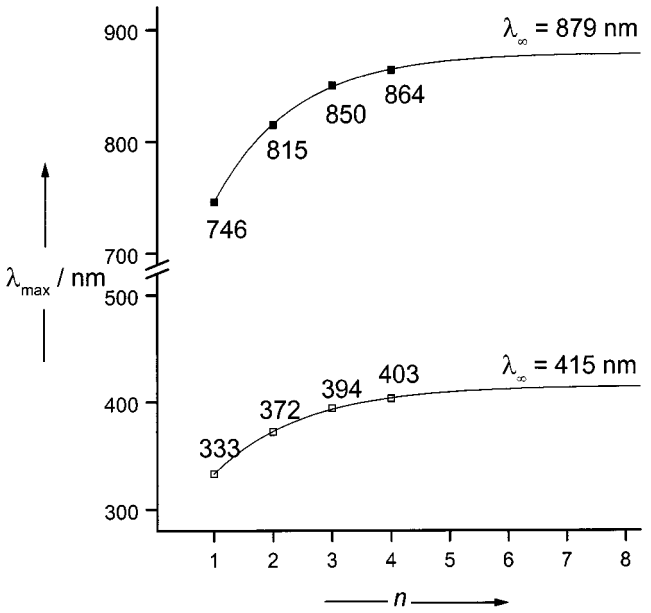
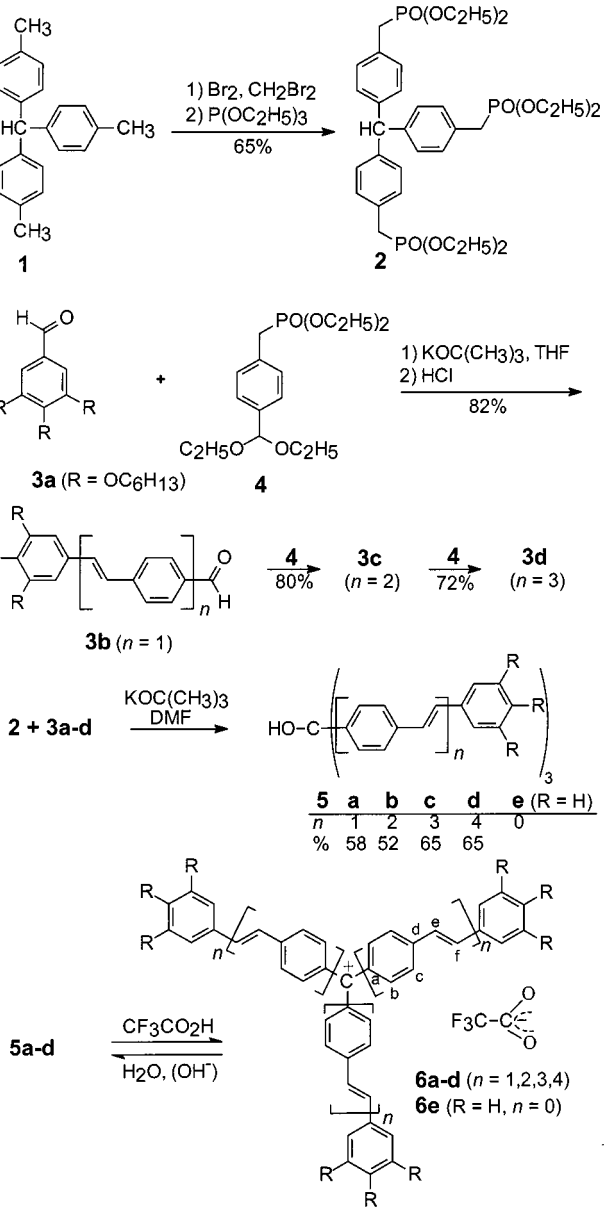


Figure 2. Maxima of the long wavelength absorption of the carbinols **5a**−**d** (□, measured in $CHCl_3$) and their salts **6a**−**d** (■, measured in $CHCl_3/CF_3CO_2H$, 7:3)

an algorithm based on e functions.[9,10] In both series **5** and **6** the limiting values (with an error $\Delta\lambda$ of ± 1 nm) are reached for the effective conjugation length $n_{ECL} = 8$. Due to possible interactions between the OPV chains, this value is smaller than in a single OPV chain, where n_{ECL} amounts to between 10 and 11.[9]

The conjugation in the ground state of the ions **6a**−**d** can be judged by the corresponding ^{13}C NMR spectroscopic data, which reflect the charge distribution. The transformation of the unsubstituted triphenylcarbinol **5e** to the corresponding triphenylmethylium ion **6e** (Scheme 1) leads to a low-field shift of the signal of the central carbon atom of $\Delta\delta = 131.7$ ppm; the *o*- and *p*-C atoms of the benzene rings show low-field shifts of 15.8 and 17.8 ppm, respectively. In particular, the *p*-C atoms are a good indicator for partial charges.[11] Irrespective of the length of the OPV chain, the formation of **6a**−**d** from **5a**−**d** provokes an even stronger delocalisation of the charge in comparison to **5e** → **6e**. Accordingly, the low-field shifts $\Delta\delta$ amount only to 109.9 ppm for the central carbon atom and to 12.5, 14.2 and 9.1 ppm for the carbon atoms b, d and f, respectively (Table 1 and Scheme 1). The alternating effect, which consists of a low-field shift of every second carbon atom, is in accordance with the classical theory of resonance structures. The effect decreases in the OPV chains with increasing distance of the measured C atom from the methylium centre. The other carbon atoms exhibit small effects, except the *ipso*-C bound to the central carbon atom, which is shifted by $\Delta\delta = (-7 \pm 1)$ ppm to higher field on going from **5a**−**d** to **6a**−**d**. The charge distribution in the ground state and the until-now unknown charge distribution in the excited state are certainly important features for the electronic transition, which has charge transfer character.[12]



Scheme 1. Preparation of the carbinols **5a**−**d** with OPV chains and transformation of **5a**−**d** and the model compound **5e** to the corresponding methylium salts **6a**−**e**

Table 1. Selected ^{13}C NMR spectroscopic data of the carbinols **5a**−**d** ($CDCl_3$) and their methylium ions **6a**−**d** ($CDCl_3/F_3CCOOD$, 7:3); the values of the unsubstituted systems triphenylcarbinol **5e** and its cation **6e** are included for comparison; the $\Delta\delta$ values represent the signal shifts observed for the transformation **5** → **6**

Compound		Central C atom	Inner styrene units		
			b	d	f
5e	δ	81.9	127.8	127.1	
6e	δ	213.6	143.6	144.6	
	Δδ	131.7	15.8	17.5	
5a−**d**	δ	81.5 ± 0.3	128.1 ± 0.2	136.4 ± 0.3	128.5 ± 0.5
6a−**d**	δ	191.4 ± 0.8	140.6 ± 0.2	150.8 ± 0.5	137.6 ± 0.9
	Δδ	109.9 ± 1.1	12.5 ± 0.4	14.2 ± 0.5	9.1 ± 1.1

Conclusion

Carbinols with three OPV chains were obtained by Wittig−Horner reactions of a threefold phosphonate and stilbenoid compounds with a terminal formyl group. Treatment with strong acids leads to the corresponding methylium ions which exhibit a strong bathochromic shift of the absorption. Due to the extension of the conjugation, the absorption maxima are shifted from the visible region into the NIR. The ^{13}C NMR spectra reveal a far-reaching charge distribution.

Experimental Section

General: The melting points were measured on a Büchi melting point apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra were recorded on Bruker spectrometers AM 400 and AC 200 with $CDCl_3$ or [D_8]THF as solvent, unless otherwise noted, with TMS as internal standard. The mass spectra were obtained on a Finnigan Mat 95. A Beckman Accub 4 spectrometer served for the measurement of the IR spectra. UV/Vis spectra were taken on a Zeiss MCS 320/ 340 spectrometer. Silica gel (E. Merk 60, 70−230 mesh ASTM) was used for column chromatography. Elemental analyses were performed in the microanalytical laboratory of the Institute of Organic Chemistry of the University of Mainz, Germany.

Tris(4-methylphenyl)methane (1): The preparation can be performed by reduction of chlorotris(4-methylphenyl)methane with $LiAlH_4$ in diethyl ether[13] or simply by reduction of the chloro compound in dry ethanol. Refluxing of the chloro compound (10.0 g, 32.1 mmol) in 50 mL of ethanol for 48 h gave 8.75 g (98%) of **1** as a colorless oil. − ^1H NMR ($CDCl_3$): δ = 2.35 (s, 9 H, CH_3), 5.48 (s, 1 H, CH), 7.04/7.12 (AA′BB′, 12 H, aromat. H). − ^{13}C NMR ($CDCl_3$): δ = 21.0 (CH_3), 55.8 (CH), 129.0/129.6 (aromat. CH), 135.7/141.4 (aromat. C_q).

Diethyl Benzyl-4-{bis[4-(diethoxyphosphorylmethyl)phenyl]methyl}-phosphonate (2): Compound **1** (10.0 g, 34.9 mmol) was refluxed in 100 mL of dibromomethane for 30 min before bromine (6.0 mL, 18.7 g, 117 mmol) in 10 mL of dibromomethane was added dropwise within 2 h. After refluxing for 24 h, the reaction mixture was poured onto crushed ice. The organic phase was washed with saturated $NaHCO_3$ solution and water and dried over Na_2SO_4. The volatile components were evaporated. The crude product was dissolved in hot petroleum ether (40−70 °C) and the precipitate directly used for the following step, where it was heated in triethyl phosphite (17.45 g, 105 mmol) for 8 h at 150 °C. The generated bromoethane was removed during the reaction and the unreacted triethyl phosphite distilled off at the end. Yield 15.8 g (65%), yellowish oil. − IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1}, 2900, 1650, 1510, 1390, 1240, 1150, 960, 760, 660. − ^1H NMR ($CDCl_3$): δ = 1.16 (t, 18 H, CH_3), 3.05 (d, $^2J_{H,P}$ = 21.4 Hz, 6 H, CH_2P), 3.94 (m, 12 H, OCH_2), 5.40 (s, 1 H, HC), 6.95/7.13 (AA′BB′, 12 H, aromat. H). − ^{13}C NMR ($CDCl_3$): δ = 16.2 (CH_3), 33.3 (d, ^1J = 139.5 Hz, CH_2P), 55.7 (CH), 129.5, 129.7 (aromat. CH), 142.4, 142.4 (aromat. C_q). − MS (FD): *m/z* (%) = 695 (100) [$M^{+\cdot}$]. − $C_{34}H_{49}O_9P_3$ (694.7): calcd. C 58.78, H 7.11; found C 58.79, H 7.11.

The aldehyde **3a**, the phosphonate **4** and the aldehyde **3b** were prepared according to procedures described in the literature.[7]

all-(*E*)-4-(2-{Phenyl-4-[2-(3,4,5-trihexyloxyphenyl)ethenyl]}-ethenyl)benzaldehyde (3c): Compounds **3b** (10.17 g, 20.0 mmol) and **4** (6.61 g, 20.0 mmol) dissolved in 50 mL of dry THF were dropped into a solution of potassium *tert*-butoxide (4.49 g, 40.0 mmol) in 35 mL of dry THF. The mixture was stirred at room temperature for 12 h and then poured onto 100 g of crushed ice. Treatment with 10 mL of 2 M hydrochloric acid and 100 mL of $CHCl_3$ led to the deprotected aldehyde dissolved in the organic layer. The crude product was purified by filtration over silica gel [10 × 12 cm, acetone/petroleum ether (40−70 °C) 1:15] and recrystallized from hot $CHCl_3$ to which ethanol was added till the solution became turbid. Yield: 9.74 g (80%), yellow crystals, m.p. 73 °C. − IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1}, 2960, 2940, 1690, 1590, 1570, 1500, 1460, 1430, 1380, 1340, 1260, 1240, 1170, 1130, 1110, 1020, 960, 840, 790. − ^1H NMR ($CDCl_3$): δ = 0.89 (m, 9 H, CH_3), 1.32−1.48 (m, 18 H, CH_2), 1.77 (m, 6 H, CH_2), 3.96 (t, 2 H, OCH_2), 4.01 (t, 4 H, OCH_2), 6.70 (s, 2 H, aromat. H), 6.95/7.03 (AB, ^3J = 16.1 Hz, 2 H, olefin H, donor side), 7.12/7.23 (AB, ^3J = 16.1 Hz, 2 H, olefin H, acceptor side), 7.49/7.50 (AA′BB′, 4 H, aromat. H, central ring), 7.63/7.85 (AA′BB′, 4 H, aromat. H, acceptor side), 9.97 (s, 1 H, CHO). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6−31.8 (CH_2, partly superimposed), 69.4 (OCH_2), 73.5 (OCH_2), 105.6, 126.7, 126.8, 126.9, 127.0, 127.2, 129.4, 130.2, 131.7 (aromat. and olefin CH), 132.4, 135.4, 135.7, 137.8, 138.8 143.5, 153.4 (aromat. C_q), 191.4 (CHO). − MS (FD): *m/z* (%) = 610 (100) [$M^{+\cdot}$]. − $C_{41}H_{54}O_4$ (610.9): calcd. C 80.61, H 8.91; found C 80.59, H 8.93.

all-(*E*)-4-{2-[Phenyl-4-(2-{phenyl-4-[2-(3,4,5-trihexyloxyphenyl)-ethenyl]}ethenyl)]ethenyl}benzaldehyde (3d): The preparation was performed as described for **3c**. Yield 72%, yellow crystals, m.p. 164 °C. − IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1}, 2840, 1690, 1580, 1490, 1460, 1420, 1380, 1340, 1230, 1160, 1110, 960, 840, 790, 720. − ^1H NMR ($CDCl_3$): δ = 0.89 (t, 9 H, CH_3), 1.28−1.48 (m, 18 H, CH_2), 1.79 (m, 6 H, CH_2), 3.94−4.03 (m, 6 H, OCH_2), 6.71 (s, 2 H, aromat. H), 6.93/7.04 (AB, ^3J = 16.1 Hz, 2 H, olefin H, donor side), 7.11 ("s", 2 H, olefin H, middle), 7.13/7.21 (AB, ^3J = 16.1 Hz, olefin H, acceptor side), 7.48−7.51 (m, 8 H, aromat. H), 7.63/7.84 (AA′BB′, 4 H, aromat. H, acceptor side), 9.97 (s, 1 H, CHO) − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6, 25.8, 29.5, 30.3, 31.8 (CH_2, CH_2 partly superimposed), 69.6 (OCH_2), 73.6 (OCH_2), 105.5, 126.8, 126.9, 127.0, 127.3, 130.3 (aromat. CH), 127.2, 127.9, 128.9, 129.1, 131.3−138.7 (olefin CH and aromat. C_q, partly superimposed), 143.5 (C_q), 153.4 (C_q), 191.5 (CHO). − MS (FD): *m/z* (%) = 712 (100) [$M^{+\cdot}$]. − $C_{49}H_{60}O_4$ (713.0): calcd. C 82.54, H 8.48; found C 82.52, H 8.46.

all-(*E*)-Tris{Phenyl-4-[2-(3,4,5-trihexyloxyphenyl)ethenyl]}methanol (5a): The preparation was performed as described for **3c**. The reaction time at room temperature was 2 days. The crude product was purified by column filtration (10 × 13 cm silica gel, $CHCl_3$). Yield: 58%, oil. − IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2840, 1570, 1490, 1460, 1420, 1370, 1340, 1310, 1220, 1110, 960, 920, 820, 720, 700, 640. − ^1H NMR ($CDCl_3$): δ = 0.89 (t, 27 H, CH_3), 1.30−1.47 (m, 54 H, CH_2), 1.69−1.83 (m, 18 H, CH_2), 3.93−4.01 (m, 18 H, OCH_2), 6.68 (s, 6 H, aromat. H), 6.94/ 6.99 (AB, ^3J = 16.1 Hz, 6 H, olefin H), 7.27/7.43 (AA′BB′, 12 H, aromat. H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6−31.8 (CH_2, superimposed), 69.3, 73.5 (OCH_2), 81.2 (C_qOH), 105.2, 125.6, 128.0 (aromat. CH), 126.9, 128.9 (olefin CH), 132.3, 136.1, 138.3, 145.9, 153.1 (aromat. C_q). − UV ($CHCl_3$): λ_{max} (log ε) = 333 nm (4.9). − MS (FD): *m/z* (%) = 1468 (100) [$M^{+\cdot}$]. − $C_{97}H_{142}O_{10}$ (1468.2): calcd. C 79.35, H 9.75; found C 79.29, H 9.72.

all-(*E*)-Tris[phenyl-4-(2-{phenyl-4-[2-(3,4,5-trihexyloxyphenyl)-ethenyl]}ethenyl)]methanol (5b): Preparation analogous to **5a**. The crude product was dissolved in chloroform and precipitated by adding ethanol. Yield: 52%, m.p. 80 °C. − IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1},

2920, 2840, 1650, 1570, 1500, 1460, 1420, 1380, 1340, 1260, 1110, 1020, 960, 800. − ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 27 H, CH_3), 1.32−1.49 (m, 54 H, CH_2), 1.72−1.85 (m, 18 H, CH_2), 3.96−4.02 (m, 18 H, OCH_2), 6.71 (s, 6 H, aromat. H), 6.95/7.02 (AB, ^3J = 16.1 Hz, 6 H, olefin H, donor side), 7.10 ("s", 6 H, olefin H), 7.30 (AA′ part of AA′BB′, 6 H, aromat. H), 7.45−7.47 (BB′ and AA′BB′, 18 H, aromat. H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6−31.8 (CH_2, superimposed), 69.4, 73.6 (OCH_2), 81.8 (C_qOH), 105.6, 126.2, 126.7, 126.9, 128.3 (aromat. CH), 127.3, 128.0, 128.8, 129.0 (olefin CH), 132.0, 136.5, 136.6, 137.0, 138.8, 146.1, 153.4 (aromat. C_q). − UV ($CHCl_3$): λ_{max} (log ε) = 372 nm (5.2). − MS (FD): *m/z* (%) = 1774 (100) [M^+]. − $C_{121}H_{160}O_{10}$ (1774.6): calcd. C 81.90, H 9.09; found C 81.85, H 9.02.

all-(*E*)-Tris(phenyl-4-{2-[phenyl-4-(2-{phenyl-4-[2-(3,4,5-trihexyloxyphenyl)ethenyl]}ethenyl)]ethenyl})methanol (5c): The preparation was performed according to the procedure described for **5a**. The reaction time amounted to 3 days. The crude product was dissolved in chloroform and precipitated by the addition of ethanol. Yield 65%, m.p. 175 °C. − IR (KBr): ṽ: = 2940 cm^{-1}, 2920, 2830, 1565, 1530, 1490, 1450, 1420, 1370, 1330, 1250, 1225, 1105, 1105, 1005, 960, 915, 830, 720, 620. − ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 27 H, CH_3), 1.32−1.49 (m, 54 H, CH_2), 1.72−1.85 (m, 18 H, CH_2), 3.69−4.02 (m, 18 H, OCH_2), 6.71 (s, 6 H, aromat. H), 6.95/7.02 (AB, ^3J = 16.1 Hz, 6 H, olefin H, donor side), 7.10 ("s", 12 H, olefin H), 7.29−7.49 (m, 36 H, aromat. H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6−31.8 (CH_2, superimposed), 69.4, 73.6 (OCH_2), 81.8 (C_qOH), 105.5, 126.2, 126.8−127.0, 127.3, 128.1, 128.3, 128.7, 129.0 (aromat. and olefin CH, partly superimposed), 132.6, 136.6−136.9, 138.7, 146.1, 153.4 (aromat. C_q, partly superimposed). − UV ($CHCl_3$): λ_{max} (log ε) =394 nm (5.4). − MS (FD): *m/z* (%) = 2080 (100) [M^+]. − $C_{145}H_{178}O_{10}$ (2081.0): calcd. C 83.69, H 8.62; found C 83.67, H 8.59.

all-(*E*)-Tris{phenyl-4-[2-(phenyl-4-{2-[phenyl-4-(2-{4-[2-(3,4,5-trihexyloxyphenyl)ethenyl]}ethenyl)]ethenyl})ethenyl]}methanol (5d): Preparation and purification analogous to **5c**. Yield 65%, m.p. >300 °C. − IR (KBr): ṽ = 3400 cm^{-1}, 3000, 2920, 2900, 2840, 1565, 1530, 1495, 1450, 1415, 1370, 1330, 1245, 1220, 1120, 1100, 1105, 960, 915, 830, 785, 720, 690. − ^{1}H NMR ([D_8]THF): δ = 0.89 (t, 27 H, CH_3), 1.32−1.55 (m, 54 H, CH_2), 1.71−1.85 (m, 18 H, CH_2), 3.94−4.02 (m, 48 H, OCH_2), 6.82 (s, 6 H, aromat. H), 7.05/ 7.12 (AB, ^3J = 16.1 Hz, 6 H, olefin H, donor side), 7.21 (m, 18 H, olefin H), 7.35−7.56 (m, 48 H, aromat. H). − ^{13}C NMR ([D_8]THF): δ = 14.0 (CH_3), 22.6−31.8 (CH_2, superimposed), 69.4, 73.6 (OCH_2), 81.8 (C_qOH), 105.5, 126.3−129.1 (aromat. and olefin CH, superimposed), 132.6, 136.6−136.9, 138.6, 146.1, 153.3 (aromat. C_q, partly superimposed). − UV ($CHCl_3$): λ_{max} (log ε) = 403 nm (5.5). − MS (FD): *m/z* (%) = 2387 (100) [M^+]. − $C_{169}H_{196}O_{10}$ (2387.4): calcd. C 85.02, H 8.28; found C 85.42, H 7.98.

Generation of the Methylium Trifluoroacetates 6a−d: The carbinols **5a−d** (about 50 mg) were dissolved in chloroform/trifluoroacetic acid (7:3; about 0.7 mL). A spontaneous and quantitative formation of the salts **6a−d** occurred.

all-(*E*)-Tris{phenyl-4-[2-(3,4,5-trihexyloxyphenyl)ethenyl]}methylium Trifluoroacetate (6a): ^{1}H NMR ($CDCl_3/CF_3CO_2D$, 7:3): δ = 0.91 (m, 27 H, CH_3), 1.32−1.49 (m, 54 H, CH_2), 1.81 (m, 18 H, CH_2), 4.08 (t, 12 H−OCH_2), 4.16 (t, 6 H, *p*-OCH_2), 6.88 (s, 6 H, aromat. H),[14] 7.20 (A part of olefin AB, ^3J = 16.1 Hz, 3 H, H_e),[15] 7.55 (B of AB, ^3J = 16.1 Hz, 3 H, H_f), 7.61 (AA′ part of AA′BB′, 6 H, H_c), 7.86 (BB′ of AA′BB′, 6 H, H_b). − ^{13}C NMR ($CDCl_3/CF_3CO_2D$ 7:3): δ = 13.6, 13.7 (CH_3), 22.3, 22.4, 25.3, 25.5, 29.0, 29.5, 31.3, 31.4 (CH_2), 69.6 (*m*-OCH_2), 75.1 (*p*-OCH_2), 106.8 (aromat. CH),[14] 126.0 (olefin HC_e), 127.8 (aromat. HC_c), 132.0 (aromat. C_q), 138.4 (olefin HC_f), 138.6 (aromat. C_a), 138.9 (*p*-C_qO), 140.5 (aromat. HC_b), 150.4 (aromat. C_d), 152.9 (*m*-C_qO), 192.2 (central C). − Vis ($CHCl_3$): λ_{max} (log ε) = 746 nm (4.9).

all-(*E*)-Tris[phenyl-4-(2-{phenyl-4-[2-(3,4,5-trihexyloxyphenyl)ethenyl]}ethenyl)]methylium Trifluoroacetate (6b): ^{1}H NMR ($CDCl_3/CF_3CO_2D$, 7:3): δ = 0.90 (m, 27 H, CH_3), 1.29−1.47 (m, 54 H, CH_2), 1.79 (m, 18 H, CH_2), 4.08 (t, 12 H−OCH_2), 4.13 (t, 6 H, *p*-OCH_2), 6.82 (s, 6 H, aromat. H),[14] 7.02/7.12 (AB, ^3J = 16.1 Hz, 6 H, olefin H), 7.35 (A part of olefin AB, ^3J = 16.1 Hz, 3 H, H_e), 7.66 (B of AB, superimposed, 3 H, H_f), 7.58−7.67 (m, 18 H, aromat. H), 7.88 (m, 6 H, H_b). − ^{13}C NMR ($CDCl_3/CF_3CO_2D$, 7:3): δ = 13.5, 13.5 (CH_3), 22.3, 22.3, 25.2, 25.5, 28.9, 29.3, 31.3, 31.4 (CH_2), 69.8 (*m*-OCH_2), 75.3 (*p*-OCH_2), 105.5 (aromat. CH),[14] 126.0 (olefin HC_e), 126.4, 127.2, 127.8, 128.5, 130.2 (aromat. and olefin CH), 133.7, 134.9, 136.1 (aromat. C_q), 138.3 (olefin HC_f), 138.9 (*p*-C_qO), 139.8 (C_a), 140.4 (HC_b), 150.5 (C_d), 152.4 (*m*-C_qO), 192.2 (central C). − NIR ($CHCl_3$): λ_{max} (log ε) = 815 nm (5.0).

all-(*E*)-Tris(phenyl-4-{2-[phenyl-4-(2-{phenyl-4-[2-(3,4,5-trihexyloxyphenyl)ethenyl]}ethenyl)]ethenyl})methylium Trifluoroacetate (6c): ^{1}H NMR ($CDCl_3/CF_3CO_2D$, 7:3): δ = 0.88 (m, 27 H, CH_3), 1.27−1.48 (m, 54 H, CH_2), 1.79 (m, 18 H, CH_2), 4.06 (t, 12 H−OCH_2), 4.10 (t, 6 H, *p*-OCH_2), 6.74 (s, 6 H, aromat. H),[14] 6.97/ 7.03 (AB, ^3J = 16.0 Hz, 6 H, olefin H), 7.15/7.22 (AB, ^3J = 16.1 Hz, 6 H, olefin H), 7.33 (A part of olefin AB, ^3J = 16.1 Hz, 3 H, H_e), 7.61 (B of AB, superimposed, 3 H, H_f), 7.50−7.67 (m, 30 H, aromat. H), 7.87 (m, 6 H, H_b). − ^{13}C NMR ($CDCl_3/CF_3CO_2D$, 7:3): δ = 13.8, 13.8 (CH_3), 22.4, 22.4, 25.3, 25.6, 29.1, 29.4, 31.4, 31.5 (CH_2), 69.5 (*m*-OCH_2), 74.9 (*p*-OCH_2), 105.2 (aromat. CH),[14] 126.0 (olefin HC_e), 126.8, 127.1, 127.2, 127.6, 127.8, 127.8, 128.0, 128.6, 130.3 (aromat. and olefin CH), 133.7, 134.9, 136.0, 136.3, 137.1 (aromat. C_q), 138.3 (olefin HC_f), 138.8 (*p*-C_qO), 140.0 (C_a), 140.4 (HC_b), 150.3 (C_d), 152.6 (*m*-C_qO), 190.6 (central C). − NIR ($CHCl_3$): λ_{max} (log ε) = 850 nm (5.1).

all-(*E*)-Tri{phenyl-4-[2-(phenyl-4-{2-[phenyl-4-(2-{phenyl-4-[2-(3,4,5-trihexyloxyphenyl)ethenyl]}ethenyl)]ethenyl})ethenyl]}methylium Trifluoroacetate (6d): − ^{1}H NMR ($CDCl_3/CF_3CO_2D$, 7:3): δ = 0.89 (m, 27 H, CH_3), 1.25−1.46 (m, 54 H, CH_2), 1.79 (m, 18 H, CH_2), 4.08 (m, 18 H, OCH_2), 6.76 (s, 6 H, aromat. H),[14] 7.01−7.28 (m, 28 H, olefin H), 7.40−7.62 (m, 42 H, aromat. H and H_f), 8.06 (m, 6 H, H_b). − ^{13}C NMR ($CDCl_3/CF_3CO_2D$, 7:3): δ = 13.9, 13.9 (CH_3), 22.5, 22.7, 25.8, 25.8, 29.2, 29.5, 31.5, 31.6 (CH_2), 69.8 (*m*-OCH_2), 75.3 (*p*-OCH_2), 105.5 (aromat. CH),[14] 126.2 (olefin HC_e), 126.6−131.0 (aromat. and olefin CH, superimposed), 134.4−138.4 (aromat. C_q, superimposed), 136.8 (olefin HC_f), 139.5 (*p*-C_qO), 140.3 (C_a), 140.8 (HC_b), 150.5 (C_d), 152.6 (*m*-C_q), 191.5 (central C). − NIR ($CHCl_3$):[16] λ_{max} = 850 nm.

Isolation of all-(*E*)-Tris{phenyl-4-[2-(3,4,5-trihexyloxyphenyl)-ethenyl]}methylium Tetrafluoroborate (6a′): The carbinol **5a** (50 mg, 3.4×10^{-2} mmol) was dissolved in 30 mL of CH_2Cl_2 and treated with 2 mL of HBF_4 and ca. 2 mL of acetic anhydride, until the salt **6a′** precipitated quantitatively as a dark blue solid. The filtered compound was purified by evaporation of the volatile parts in vacuo (10^2 Pa). The salt is highly hygroscopic; it cannot be handled in air and hydrolyses rapidly in aqueous solvents.

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[16] Due to the hygroscopic behavior an exact determination of ε failed.

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