

Dendritic Triphenylmethylium and Tetraphenylmethane Compounds

Herbert Meier,* Soungkyoo Kim, Annette Oehlhof

Institute of Organic Chemistry, University of Mainz, Duesbergweg 10-14, 55099 Mainz, Germany

Fax +49(6131)39225396; E-mail: hmeier@mail.uni-mainz.de

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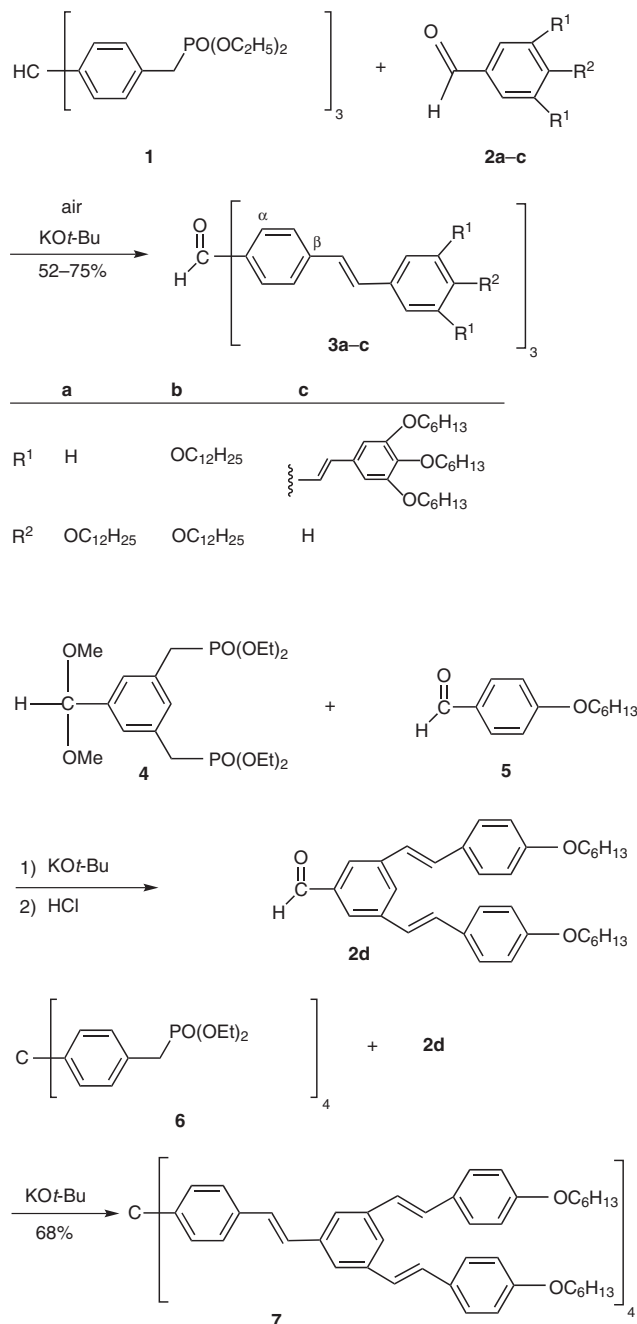
Abstract: Stilbenoid dendrimers possessing a methanol or methane core are prepared using Wittig–Horner reactions. The dendritic tris(stilbenyl)carbinols **3a–c** are converted into the corresponding methylium salts **3'a–c** on treatment with trifluoroacetic or tetrafluoroboric acid. The extended cross-conjugation in the dendritic methylium ion **3'c** results in a long-wavelength absorption ($\lambda_{\text{max}} = 697$ nm) whereas the conjugated model systems **3'a** and **3'b** are red-shifted ($\lambda_{\text{max}} = 772$ nm and 748 nm, respectively). Charge delocalization in the cations is evident from the low-field shifts of the ^{13}C NMR signals. In contrast to the dark-blue dyes **3'a–c**, the tris(stilbenyl)carbinols and tetrakis(stilbenyl)methane derivatives **3a–c** and **7** exhibit long-wavelength absorption bands in the UV region.

Key words: stilbene, charge delocalization, Wittig–Horner reaction, olefination, dendrimers, dyes

From photophysical and photochemical viewpoints, stilbene-containing molecules are a well-studied class of compounds.¹ Therefore, dendrimers possessing stilbenoid building blocks represent an attractive area of research.² A number of dendritic structures, in which the dendrons (but not the core) consist of stilbene building blocks, have been described.³

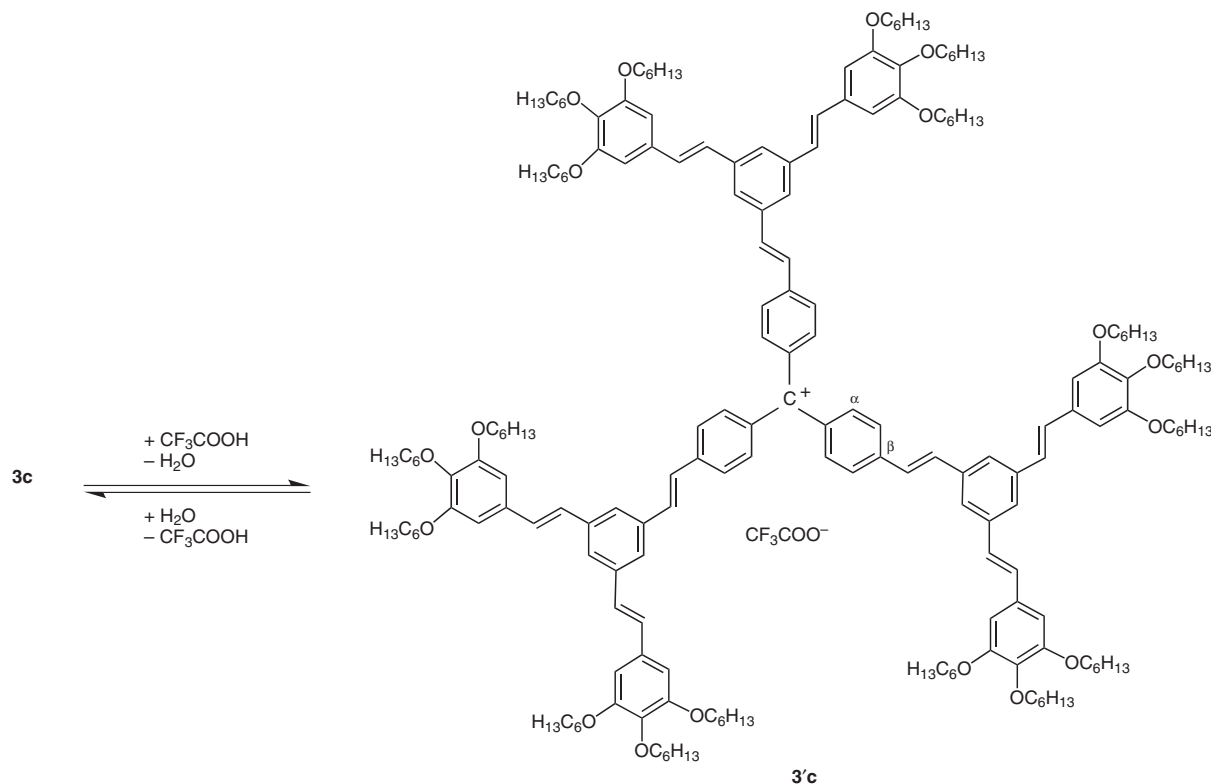
We report here on novel stilbenoid dendrimers containing triphenylmethylium or tetraphenylmethane cores. The dendrons of these compounds represent extended π -systems in which full conjugation is blocked by a saturated center ($\text{sp}^3\text{-C}$) or is 'opened' by a carbenium center ($\text{sp}^2\text{-C}^+$). Peripheral alkoxy groups serve as solubilizing groups, and moreover, as electron-donor groups which impart the methylium systems with acceptor–donor character (AD_3).⁴

Preparation of the target dendrimers **3a–c** and **7** was started from the triphosphonate **1**⁵ or the tetraphosphonate **6**,⁶ (Scheme 1). Wittig–Horner reactions of **1** and aldehyde **2c**, and **6** with aldehyde **2d**, yielded the desired products **3c** (52%) and **7** (68%), respectively. The star-shaped model compounds **3a** (70%) and **3b** (75%) were prepared via analogous reactions of triphosphonate **1** with aldehydes **2a** and **2b**, respectively. The substrate aldehydes **2a**,^{7,8} **2b**,^{7,9} **2c**^{10,11} and **2d** contain long, flexible alkoxy chains. Aldehyde **2d** was obtained in 82% yield analogously to **2c** by reaction of diphosphonate **4**, which contains a formyl group protected as a dimethylacetal, with 4-(hexyloxy)benzaldehyde (**5**).¹⁰



Scheme 1 Preparation of the dendrimers **3c** and **7** and the model compounds **3a** and **3b**

The Wittig–Horner olefinations gave the expected products in *cis/trans* ratios of about 5:95. After purification by crystallization, the amount of *cis* isomers still present was



Scheme 2 Formation and hydrolysis of the dendritic triphenylmethylium salt **3'c**

less than 2%. The detection limit for *cis*-configured double bonds in our study was 2%, and hence we were unable to detect any *cis*-configured dendrimers in our products. This was found to be the case for the solid products **3a**, **3c** and **7**, as well as for the oily product **3b** which was purified by column chromatography on silica gel.

Treatment of the carbinols **3a–c** with trifluoroacetic acid led to elimination of water and formation of the corresponding triphenylmethylium trifluoroacetates **3'a–c**. In order to shift the equilibrium to favour the salts **3'a–c**, we used a large excess of trifluoroacetic acid (molar ratio of 3/acid = 1:200) (Scheme 2).

Table 1 summarizes the key ^{13}C NMR data for the transformations of **3a–c** into salts **3'a–c**. For comparison, we have included the corresponding ^{13}C NMR data for triphenylcarbinol (Ph_3COH) and its cation (Ph_3C^+).⁵ The ^{13}C chemical shifts are highly sensitive towards changes in the partial charges. The formation of the triphenylmethylium ions is apparent from the strong low-field shift of the signal due to the central carbon atom (C^+). The $\Delta\delta$ value of $\text{Ph}_3\text{COH}/\text{Ph}_3\text{C}^+$ is 131.7 ppm. The corresponding $\Delta\delta$ values of **3a–c**/**3'a–c** decrease in the order **3c** > **3b** > **3a** (120.8, 111.1 and 109.2 ppm, respectively). This trend results from the increasing delocalization of the positive charge. The *meta*-branching in dendrimer **3'c** is less suited to charge delocalization than the linear conjugation present in **3'a,b**. Therefore, dendrimers **3c/3'c** exhibit the highest $\Delta\delta$ value. Charge delocalization occurs over the whole ion, but the major effect is apparent at the *ortho*-

Table 1 Selected ^{13}C NMR Data of Carbinols **3a–c** in CDCl_3 and Their Corresponding Triphenylmethylium Ions **3'a–c** in CDCl_3 – CF_3COOD (7:3)

Compound		Central ^a C^+	α -C ^a	β -C ^a
3a	δ	81.8	128.3	136.9
3'a	δ	191.0	140.3	150.9
	$\Delta\delta$	109.2	12.0	14.0
3b	δ	81.8	128.3	136.6
3'b	δ	192.9	140.6	150.5
	$\Delta\delta$	111.1	12.3	13.9
3c	δ	82.3	128.3	136.4
3'c	δ	203.1	140.8	150.7
	$\Delta\delta$	120.8	12.5	14.3
Ph_3COH^b	δ	81.9	127.8	127.1
$\text{Ph}_3\text{C}^+{}^b$	δ	213.6	143.6	144.6
	$\Delta\delta$	131.7	15.8	17.5

^a The positions of C^+ , α -C and β -C are shown in Scheme 2.

^b The corresponding ^{13}C chemical shifts of Ph_3COH and cation Ph_3C^+ are included for comparison.

and *para*-positions (α and β) of the benzene rings adjacent to the central carbon atom (Scheme 2 and Table 1).

Apart from small effects due to the medium, the ^1H and ^{13}C NMR data of dendrimer **7** are the same in CDCl_3 and $\text{CDCl}_3\text{--CF}_3\text{COOD}$ (7:3).

The tris(stilbenyl)carbinols **3a–c** and tetrakis(stilbenyl)methane **7** show long-wavelength electron transitions in the UV region at about 330 nm in CHCl_3 . Dendrimer **3c** has, for example, a λ_{max} value of 329 nm ($\epsilon = 112350 \text{ L mol}^{-1}\text{cm}^{-1}$) and dendrimer **7** has a λ_{max} value of 327 nm ($\epsilon = 151950 \text{ L mol}^{-1}\text{cm}^{-1}$).

The saturated sp^3 center in **3a–c** and **7** prevents the systems being fully conjugated whilst homoconjugation has a comparably small effect. The obtained ϵ values indicate the presence of three and four more or less independent chromophores in **3a–c** and **7**, respectively.

Formation of the methylium dye **3c** \rightarrow **3'c** shifts the UV band into the visible region ($\lambda_{\text{max}} = 697 \text{ nm}$) because the central sp^2 carbon atom allows cross-conjugation of the dendrons. Interestingly, the bathochromic shift resulting from formation of methylium ion **3'a** is larger ($\lambda_{\text{max}} = 772 \text{ nm}$). Apart from the 'opened' conjugation through the center, each 'arm' of **3'a** has push–pull character. In principle, dendrimer **3'c** represents an AD_3 system,⁴ but due to the *meta*-branching, the intramolecular charge transfer (ICT) is much smaller in **3'c** since it is reduced to a mere inductive or field effect.

The dark blue dyes **3'a–c** could be isolated in pure solid state as tetrafluoroborates, but they are very hygroscopic, becoming sticky as they begin to hydrolyze and fade in color. Although the reaction center is sterically shielded in **3'c**, it did not exhibit higher stability towards hydration in comparison to **3'a,b**.

Melting points were measured with a Büchi melting point apparatus and are uncorrected. UV/Vis spectra were obtained with a Zeiss MCS 320/340 diode array spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker AMX 400 spectrometer at 400 MHz and 100 MHz, respectively. CDCl_3 served as solvent and TMS as internal standard, unless otherwise noted. Field desorption (FD) mass spectra were obtained with a Finnigan MAT 95 spectrometer. Elemental analyses were performed in the Microanalytical Laboratory of the Institute of Organic Chemistry of the University of Mainz. Column chromatography was carried out on silica gel (60 M, mesh 230–400, Machery-Nagel).

3,5-Bis[(E)-2-[4-(hexyloxy)phenyl]ethenyl]benzaldehyde (**2d**)

4-(Hexyloxy)benzaldehyde (**5**) (5.2 g, 25.2 mmol) was reacted with tetraethyl [5-(dimethoxymethyl)-1,3-phenylene]bis(methylene-phosphonate) (**4**) (5.6 g, 12.4 mmol) and KOt-Bu (4.0 g, 37.0 mmol) in THF (200 mL) according to a protocol for a related aldehyde.¹⁰ After 1 h at r.t., the mixture was heated at reflux for 1 h. Acid work-up using HCl (2 M, 100 mL) cleaved the acetal group. The organic layer (CHCl_3 , 200 mL) was separated, dried (MgSO_4) and evaporated to afford a residue which was crystallized from EtOH to give **2d** as colorless crystals; yield: 5.19 g (82%); mp 132 °C.

^1H NMR (400 MHz, CDCl_3): $\delta = 0.89\text{--}0.95$ (m, 6 H, CH_3), 1.30–1.40 (m, 8 H, CH_2), 1.43–1.50 (m, 4 H, CH_2), 1.74–1.82 (m, 4 H, CH_2), 3.96 (t, $^3J = 6.6 \text{ Hz}$, 4 H, OCH_2), 6.89 and 7.45 (AA'BB', 8 H, ArH, outer benzene rings), 6.97 and 7.15 (AB, $^3J = 16.2 \text{ Hz}$, 4 H,

alkene H), 7.74 (s, 1 H, ArH), 7.81 (s, 2 H, ArH), 10.02 (s, 1 H, CHO).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 14.0$ (CH_3), 22.6, 25.7, 29.2, 31.6 (CH_2), 68.2 (OCH_2), 114.9, 128.2 (CH, outer benzene rings), 124.8, 125.6, 129.4, 130.2 (Ar, alkene CH), 129.7, 137.2, 139.1, 159.4 (ArC), 192.3 (CHO).

MS (FD): m/z (%) = 510 (100) [M^+].

Anal. Calcd for $\text{C}_{35}\text{H}_{42}\text{O}_3$: C, 82.31; H, 8.29. Found: C, 82.03; H, 8.30.

Wittig–Horner Reactions; General Procedure

Triphosphonate **1**⁵ (1.0 g, 1.44 mmol) or tetraphosphonate **6**⁶ (1.0 g, 1.09 mmol) and an excess amount of the corresponding aldehyde **2a–d**^{7–11} (5.41–7.20 mmol) were dissolved in DMF (20–30 mL) and added dropwise to a suspension of KOt-Bu (2.0 g, 17.86 mmol) in DMF (30 mL) (KOH can be used as the base instead). The reaction mixture was heated at 85 °C for about 30 min and stirring was continued at r.t. for 24 h. Next, crushed ice (100.0 g) was added and the mixture extracted with CHCl_3 ($2 \times 100 \text{ mL}$). The organic phase was washed with H_2O (100 mL), dried (MgSO_4) and concentrated. The solid products **3a**, **3c** and **7** were obtained by crystallization or precipitation from CHCl_3 or EtOH. The oily product **3b** was purified by column chromatography (toluene) over silica gel.

Tris(4-[(E)-2-[4-(dodecyloxy)phenyl]ethenyl]phenyl)methanol (**3a**)

Reaction of triphosphonate **1**⁵ (1.0 g, 1.44 mmol) and aldehyde **2a**^{7,8} (1.57 g, 5.41 mmol) gave **3a**; yield: 1.13 g (70%); mp 96 °C.

^1H NMR (400 MHz, CDCl_3): $\delta = 0.87$ (t, $^3J = 6.8 \text{ Hz}$, 9 H, CH_3), 1.21–1.37 (m, 48 H, CH_2), 1.40–1.44 (m, 6 H, CH_2), 1.70–1.80 (m, 6 H, CH_2), 3.95 (t, $^3J = 6.6 \text{ Hz}$, 6 H, OCH_2), 6.86 and 7.41 (AA'BB', 12 H, ArH, outer benzene rings), 6.94 and 7.04 (AB, $^3J = 16.2 \text{ Hz}$, 6 H, alkene H), 7.26 and 7.41 (AA'BB', 12 H, ArH, inner benzene rings).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 14.0$ (CH_3), 22.6, 26.0, 29.3, 29.4, 29.4, 29.5, 29.5, 29.6, 29.6, 31.9 (CH_2), 68.2 (OCH_2), 81.8 (central C), 114.9, 125.8, 127.7, 128.3 (ArCH), 126.0, 128.7 (alkene CH), 131.8, 136.9, 145.7, 159.1 (ArC).

MS (FD): m/z (%) = 1119 (100) [M^+].

Anal. Calcd for $\text{C}_{79}\text{H}_{106}\text{O}_4$: C, 84.74; H, 9.54. Found: C, 84.69; H, 9.48.

Tris(4-[(E)-2-[3,4,5-tri(dodecyloxy)phenyl]ethenyl]phenyl)methanol (**3b**)

Reaction of triphosphonate **1**⁵ (1.0 g, 1.44 mmol) and aldehyde **2b**^{7,9} (4.71 g, 7.15 mmol) gave **3b** as a yellowish oil; yield: 2.40 g (75%).

^1H NMR (400 MHz, CDCl_3): $\delta = 0.84\text{--}0.95$ (m, 27 H, CH_3), 1.22–1.38 (m, 144 H, CH_2), 1.38–1.51 (m, 18 H, CH_2), 1.69–1.75 (m, 6 H, CH_2), 1.75–1.83 (m, 12 H, CH_2), 3.95 (t, $^3J = 6.5 \text{ Hz}$, 6 H, OCH_2 , $p\text{-OC}_{12}\text{H}_{25}$), 4.00 (t, $^3J = 6.5 \text{ Hz}$, 12 H, OCH_2 , $m\text{-OC}_{12}\text{H}_{25}$), 6.69 (s, 6 H, ArH, outer benzene rings), 6.94 and 7.00 (AB, $^3J = 16.2 \text{ Hz}$, 6 H, alkene H), 7.28 and 7.43 (AA'BB', 12 H, ArH, inner benzene rings).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 14.0$ (CH_3), 22.7, 26.1, 29.3, 29.4, 29.5, 29.7, 29.7, 30.4, 31.9 (CH_2 , partly superimposed), 69.3 (OCH_2 , $m\text{-OC}_{12}\text{H}_{25}$), 73.6 (OCH_2 , $p\text{-OC}_{12}\text{H}_{25}$), 81.8 (central C), 105.6, 126.0, 128.3 (ArCH), 127.1, 129.4 (alkene CH), 132.5, 136.6, 138.8, 145.9, 153.4 (ArC).

MS (FD): m/z (%) = 2226 (29) [M^+], 733 (100).

Anal. Calcd for $\text{C}_{145}\text{H}_{250}\text{O}_{10}$: C, 81.49; H, 11.32. Found: C, 81.38; H, 11.29.

Tris{4-[(E)-2-(3,5-bis{(E)-2-[3,4,5-tri(hexyloxy)phenyl]ethenyl}phenyl)ethenyl]phenyl}methanol (3c)

Reaction of triphosphonate **1**⁵ (1.0 g, 1.44 mmol) and aldehyde **2c**^{10,11} (6.56 g, 7.20 mmol) gave **3c**; yield: 2.24 g (52%); mp 75 °C.

¹H NMR (400 MHz, CDCl₃): δ = 0.84–0.97 (m, 54 H, CH₃), 1.24–1.40 (m, 72 H, CH₂), 1.40–1.52 (m, 36 H, CH₂), 1.71–1.78 (m, 12 H, CH₂), 1.78–1.85 (m, 24 H, CH₂), 3.96 (t, ³J = 6.5 Hz, 12 H, OCH₂, *p*-OC₆H₁₃), 4.02 (t, ³J = 6.5 Hz, 24 H, OCH₂, *m*-OC₆H₁₃), 6.73 (s, 12 H, ArH, outer benzene rings), 7.00 and 7.09 (AB, ³J = 16.1 Hz, 12 H, alkene H, outer double bonds), 7.14 and 7.20 (AB, ³J = 16.2 Hz, 6 H, alkene H, inner double bonds), 7.35 and 7.52 (AA'BB', 12 H, ArH, inner benzene rings), 7.49–7.56 (m, 9 H, ArH, central benzene rings).

¹³C NMR (100 MHz, CDCl₃): δ = 13.9, 14.0 (CH₃), 22.5, 22.6, 25.8, 25.8, 29.4, 30.3, 31.6, 31.7 (CH₂), 69.4 (OCH₂, *m*-OC₆H₁₃), 73.6 (OCH₂, *p*-OC₆H₁₃), 82.3 (central C), 105.6, 123.7, 126.2, 127.3, 128.3, 129.6, 132.3, 136.4, 137.9, 138.2, 138.7, 146.1, 153.3 (Ar, alkene CH and ArC, partly superimposed).

MS (FD): *m/z* (%) = 2982 (100) [M⁺].

Anal. Calcd for C₁₉₉H₂₈₆O₁₉: C, 80.14; H, 9.67. Found: C, 80.11; H, 9.36.

Tetrakis{4-[(E)-2-(3,5-bis{(E)-2-[4-(hexyloxy)phenyl]ethenyl}phenyl)ethenyl]phenyl}methane (7)

Reaction of tetraphosphonate **6**⁶ (1.0 g, 1.09 mmol) and aldehyde **2d** (3.34 g, 6.54 mmol) afforded **7** as a colorless solid; yield: 1.74 g (68%); mp 173 °C.

¹H NMR (400 MHz, CDCl₃): δ = 0.86–0.95 (m, 24 H, CH₃), 1.25–1.40 (m, 32 H, CH₂), 1.40–1.50 (m, 16 H, CH₂), 1.72–1.82 (m, 16 H, CH₂), 3.97 (t, ³J = 6.5 Hz, 16 H, OCH₂), 6.89 and 7.47 (AA'BB', 32 H, ArH, outer benzene rings), 6.99 and 7.12 (AB, ³J = 16.4 Hz, 16 H, alkene H, outer double bonds), 7.13–7.55 (m, 36 H, inner alkene CH, ArH, inner and central benzene rings).

¹³C NMR (100 MHz, CDCl₃): δ = 14.0 (CH₃), 22.6, 25.8, 29.3, 31.6 (CH₂), 64.5 (central C), 68.2 (OCH₂), 114.8, 123.4, 126.0, 126.3, 127.8, 128.9, 130.0, 131.5, 138.3, 138.4, 146.2, 159.1 (Ar, alkene CH, ArC, partly superimposed).

MS (FD): *m/z* (%) = 2346 (100) [M⁺].

Anal. Calcd for C₁₆₉H₁₈₈O₈: C, 86.47; H, 8.07. Found: C, 86.54; H, 8.05.

Generation of the Triphenylmethylium Cations 3'a–c

To carbinol **3a–c** (0.02 mmol) dissolved in CHCl₃ (0.7 mL) or CDCl₃ (0.7 mL), CF₃COOH (0.3 mL) or CF₃COOD (0.3 mL) was added. (This corresponds to a molar ratio of **3/acid** = 1:200). The colorless to pale yellow solutions turned deep blue immediately.

Isolation of Triphenylmethylium Tetrafluoroborates

A saturated solution of **3a** or **3c** (0.05 mmol) in CH₂Cl₂ was treated under argon with HBF₄ (3 mL) and Ac₂O (ca. 2 mL) until the corresponding dark blue salt precipitated. Filtration under argon was followed by evaporation of the volatiles in vacuo (10¹–10² Pa). The salts are highly hygroscopic and immediately become sticky and start to hydrolyze in air.

NMR and UV/Vis Characterization of Dyes 3'a–c**Tris(4-[(E)-2-[4-(dodecyloxy)phenyl]ethenyl]phenyl)methyl-ium Trifluoroacetate (3'a)**

¹H NMR [400 MHz, CDCl₃–CF₃COOD (7:3)]: δ = 0.87–0.91 (m, 9 H, CH₃), 1.31–1.55 (m, 54 H, CH₂), 1.84–1.91 (m, 6 H, CH₂), 4.21 (t, ³J = 6.4 Hz, 6 H, OCH₂), 7.08 and 7.68 (AA'BB', 12 H, ArH, outer benzene rings), 7.27 and 7.68 (AB, ³J = 16.1 Hz, 6 H, alkene H), 7.68 and 7.91 (AA'BB', 12 H, ArH, outer benzene rings).

¹³C NMR [100 MHz, CDCl₃:CF₃COOD (7:3)]: δ = 13.2 (CH₃), 22.2, 25.7, 28.9, 29.1, 29.3, 29.4, 31.3 (CH₂, partly superimposed), 69.8 (OCH₂), 116.0, 124.5, 127.6, 129.5, 129.8, 140.3 (Ar, alkene CH), 138.1, 138.8, 150.9, 160.4 (ArC), 191.0 (central C⁺).

UV/Vis: λ_{max} = 772 nm (measurement of a 7.5 × 10^{−5} M solution of **3a** and a 0.20 M solution of CF₃COOH in CHCl₃).¹²

Tris(4-[(E)-2-[3,4,5-tri(dodecyloxy)phenyl]ethenyl]phenyl)methyl-ium Trifluoroacetate (3'b)

¹H NMR [400 MHz, CDCl₃–CF₃COOD (7:3)]: δ = 0.87–0.90 (m, 27 H, CH₃), 1.25–1.55 (m, 162 H, CH₂), 1.84–1.90 (m, 18 H, CH₂), 4.16 (t, ³J = 6.5 Hz, 6 H, OCH₂, *m*-OC₁₂H₂₅), 4.25 (t, ³J = 7.0 Hz, 12 H, OCH₂, *p*-OC₁₂H₂₅), 6.97 (s, 6 H, ArH, outer benzene rings), 7.27 and 7.62 (AB, ³J = 16.2 Hz, 6 H, alkene H), 7.69 and 7.94 (AA'BB', 12 H, ArH, inner benzene rings).

¹³C NMR [100 MHz, CDCl₃–CF₃COOD (7:3)]: δ = 13.2 (CH₃), 22.3, 25.5, 25.7, 28.9, 29.1, 29.2, 29.3, 29.3, 29.4, 29.4, 29.5, 31.7 (CH₂, partly superimposed), 70.1 (OCH₂, *m*-OC₁₂H₂₅), 75.6 (OCH₂, *p*-OC₁₂H₂₅), 106.9, 126.2, 127.8, 132.4, 138.3, 138.5, 138.7, 140.6, 150.5, 152.7 (alkene CH, ArCH, ArC), 192.9 (central C⁺).

UV/Vis: λ_{max} = 748 nm (measurement of a 13.8 × 10^{−5} M solution of **3b** and a 0.53 M solution of CF₃COOH in CHCl₃).¹²

Tris(4-[(E)-2-(3,5-bis{(E)-2-[3,4,5-tri(hexyloxy)phenyl]ethenyl}phenyl)ethenyl]phenyl)methyl-ium Trifluoroacetate (3'c)

¹H NMR [400 MHz, CDCl₃–CF₃COOD (7:3)]: δ = 0.84–0.92 (m, 54 H, CH₃), 1.32–1.50 (m, 108 H, CH₂), 1.79–1.85 (m, 36 H, CH₂), 4.10–4.20 (m, 36 H, OCH₂), 6.85 (s, 12 H, ArH, outer benzene rings), 7.09 (A of AB, ³J = 16.1 Hz, 6 H, alkene H, outer double bonds), 7.17 and 7.49 (AB, ³J = 16.1 Hz, 6 H, alkene H, inner double bonds), 7.60–7.77 (m, 21 H, Ar and alkene H), 7.98 (m, 6 H, ArH).

¹³C NMR [100 MHz, CDCl₃–CF₃COOD (7:3)]: δ = 13.4 (CH₃), 22.3, 22.4, 25.7, 29.2, 30.3, 31.4 (CH₂, partly superimposed), 70.0 (OCH₂, *m*-OC₁₂H₂₅), 75.5 (OCH₂, *p*-OC₁₂H₂₅), 105.7, 125.2, 125.3, 127.8, 128.0, 129.6, 133.9, 136.0, 138.5, 138.6, 139.0, 140.8, 150.7, 152.4 (Ar, alkene CH and ArC), 203.1 (central C⁺).

UV/Vis: λ_{max} = 697 nm (measurement of a 15.8 × 10^{−5} M solution of **3c** and a 0.60 M solution of CF₃COOH in CHCl₃).¹²

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- (12) Due to the equilibration, the intensity of the band depends on the ratio of 3/CF₃COOH. The λ_{max} values are somewhat blue-shifted by a high CF₃COOH concentration. We assign this effect to a decrease of push–pull character due to increasing protonation of the alkoxy groups.