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Tris[oligo(1,4-phenylenevinylene)]methylium Dyes

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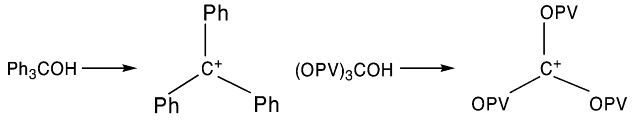
The tris[oligo(1,4-phenylenevinylene)]carbinols **2a**–**f** (n = 1–4) and the tris(4-styrylphenyl)methanes **7a**,**b** have been prepared by Wittig–Horner (**3** + **4a**–**f** → **2a**–**f**) and Siegrist reactions (**5** + **6a**,**b** → **7a**,**b**). The Wittig–Horner reactions in these examples are accompanied by an autoxidation, whereas a reduction occurs in the Siegrist reactions. Compound **2a**, the lowest member (n = 1) of the series **2a**–**d** with terminal dialkylamino groups, generates first, on treatment with acids, the methylium dye **2′a**, which absorbs far into the NIR region (λ_{max} = 1100 nm). The higher members **2b**,**c** (n = 2,3) of the carbinol series yield by acidic treatment only *N*-protonated methylium dyes **2′′′b**,**c**. The different behavior is due to a decreasing donor–acceptor interaction with increasing D–A distance. The *N*-protonated methylium salts **2′′′a**–**c** show long-wavelength absorptions in the region of the Vis/NIR border. Their values apporach, for increasing numbers n of repeat units, λ_∞ = 877 nm. The structures and possible push–pull effects of the salts **2′a** and **2′′′a**–**c** were studied by NMR and UV/Vis/NIR spectroscopy and compared with the selected model compounds **2e** and **7a**. The results shed new light on previously published triphenylmethane dyes with extended conjugation.

Introduction

Triphenylmethane dyes **1′** are a well-known class of compounds with numerous industrial applications. In recent years the strong demand for near-infrared (NIR) absorbing dyes and functional dyes for laser techniques and optoelectronics has provoked a variety of new efforts in this area.[1–4] We report herein on star-shaped systems **2′** in which the three aryl groups of **1′** are replaced by three oligo(1,4-phenylenevinylene) [OPV] chains (Figure 1). Carbinols serve as precursors in both cases.



1 **1′** **2** **2′**

Figure 1. Triphenylmethylium ions **1′** and tris[oligo(1,4-phenylenevinylene)]methylium ions **2′** and their precursor carbinols **1** and **2**.

The idea to extend the conjugation of **1′** by the introduction of *trans*-stilbene units is old,[5,6] and several tris(stilbenyl)methylium salts have been reported.[5–12] To shift the absorption far into the NIR region, the OPV chains should bear dialkylamino groups as electron-donor groups in the terminal positions. We have used bis(2-hexyloctyl)amino groups, which guarantee a good solubility even when the OPV arms are longer (n = 1–4). According to the de facto C_{3h} symmetry of such methylium ions, these disc-like systems do not have dipole moments, but they represent extended octupoles, which promise high first-order hyperpolarizabilities β (second-harmonic generation SHG) and large cross-sections for two-photon absorption (TPA).

Results and Discussion

Synthesis

The preparation of the target carbinols **2a**–**d** (n = 1–4) (Scheme 1) was based on three-fold Wittig–Horner reactions between the triphosphonate **3** and the OPV aldehydes **4a**–**d**. Carbinol **2a** (n = 1) was obtained in a yield of 68%, which corresponds to an average of 88% for each of the three olefination steps. The yields decrease with increasing numbers n of repeat units to 48% for **2b** (n = 2), 45% for **2c** (n = 3), and 8% for **2d** (n = 4). In the presence of air, no special oxidant was necessary for the formation of the carbinols **2**. Owing to the low yield of compound **2d** (n = 4), we characterized its structure by ^{1}H and ^{13}C NMR spectroscopy and its molecular mass and then excluded it from further studies.

For comparison with **2a**–**d**, which contain terminal dialkylamino groups, we synthesized the carbinols **2e**,**f** (Scheme 1) and the tris(stilbenyl)methanes **7a**,**b** (Scheme 2), all of which contain terminal alkoxy groups. Facile protonations of **2a**–**d** can occur on the central OH group and on the terminal amino groups, **2e**,**f** can be protonated on the central OH group, whereas **7a**,**b** have none of these options. The basicity of the ether groups in **2e**,**f** and **7a**,**b** is low. The

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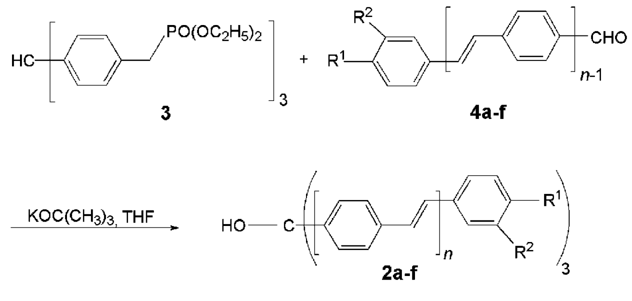
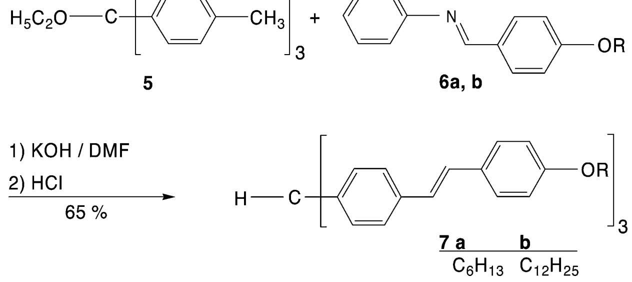


2	a	b	c	d	e	f
R^1	$N[CH_2—CH(C_6H_{13})_2]_2$				OC_6H_{13}	OC_6H_{13}
R^2	H	H	H	H	H	OC_6H_{13}
n	1	2	3	4	1	1
Yield(%)	68	48	45	8	70	65

Scheme 1. Preparation of the carbinols **2a**–**f** by three-fold Wittig–Horner reactions.

solubility of **2e** and **7a**, which bear hexyloxy groups, proved to be sufficient, so we finally selected these two compounds as model compounds for treatment with acids.



Scheme 2. Preparation of the tris(stilbenyl)methanes **7a**,**b** by three-fold Siegrist reactions.

The Siegrist reaction of ether **5** and Schiff base **6a** or **6b** yielded in a strongly alkaline medium the compounds **7a**,**b** (Scheme 2). Whereas the methine center is oxidized in the process **3**→**2**, the ether function of **5** is cleaved and reduced in the process **5**→**7**. These results reveal the high sensitivity of the trityl systems towards redox reactions.

The kinetically controlled Siegrist reaction is an extremely stereoselective *trans* olefination.[13] The Wittig–Horner olefination can lead to a small number of *cis* configurations in the stilbenoid series. Their proportion here was below the detection limit in the ^1H and ^{13}C NMR spectra (ca. 3%).

Formation of Methylium Salts

Treatment of **2a**–**c** and the selected model compound **2e** with CF_3COOH/D led to the formation of dark-blue methylium ions. Figure 2 shows the change in the ^1H and ^{13}C NMR spectroscopic data for the process **2e** + D^+ → **2′e** + HDO. The largest downfield shift is observed for the central carbon atom, which has a δ value of 81.8 ppm in **2e** and 191.0 ppm in **2′e**. This difference $\Delta\delta$ of about 109 ppm is typical for a partially delocalized positive charge. Further strong downfield shifts ($\Delta\delta$ = 12.0, 14.1, and 8.8 ppm) can be observed for the alternating positions α, β, and γ (Figure 2), which also bear partial positive charges. The polarization of the three arms is, for example, documented by the $\Delta\delta'(^{13}C)$ value of the two olefinic carbon atoms in each arm, which rises from 2.7 ppm in **2e** to 13.6 ppm in **2′e**. The methylium ion **2′e** represents a typical star-shaped donor–acceptor system AD_3.[14]

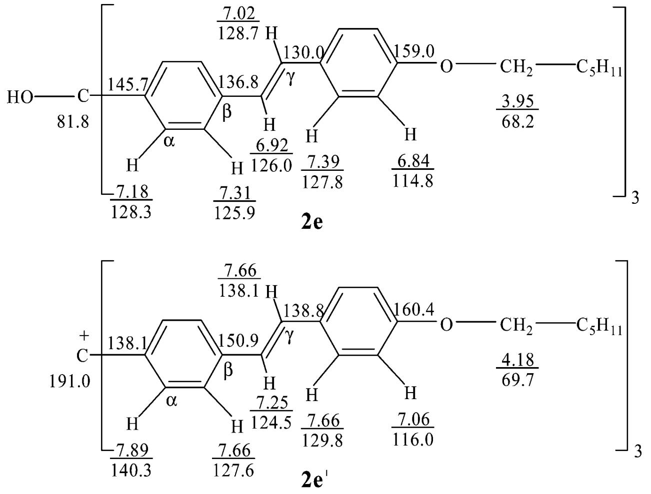
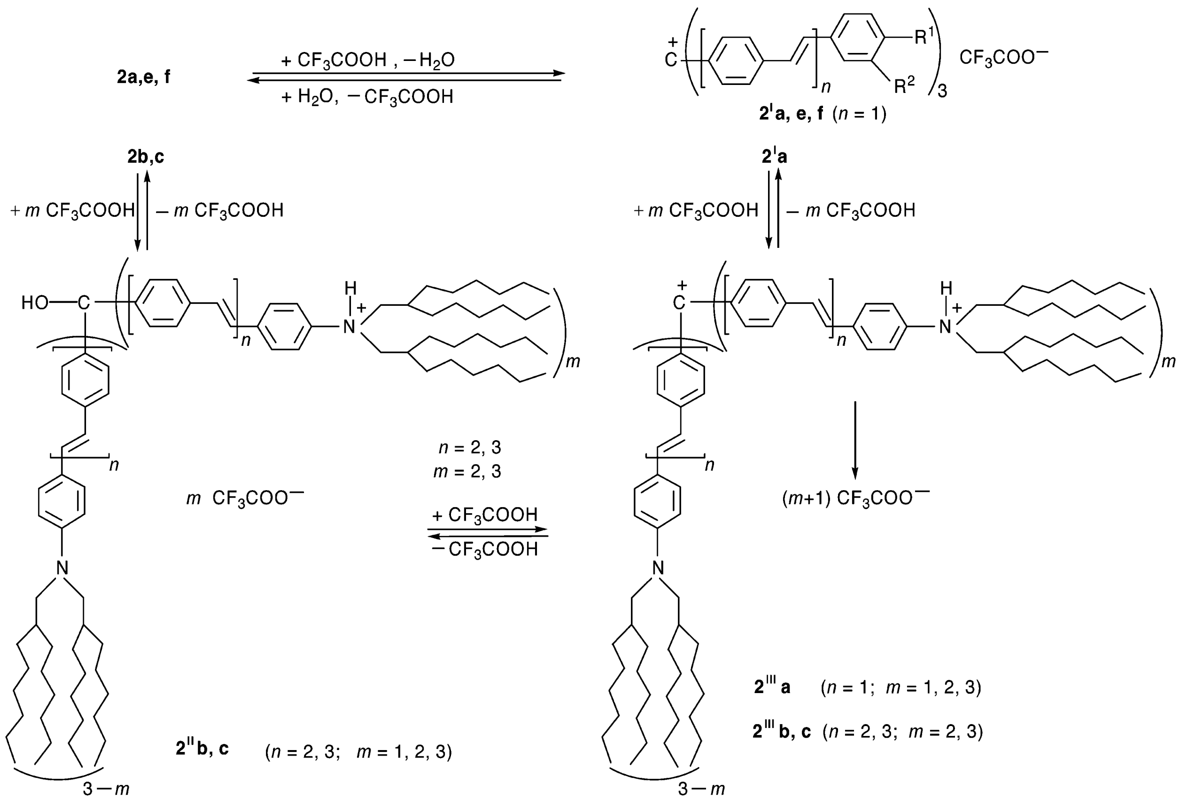


Figure 2. ^1H and ^{13}C NMR chemical shifts of **2e** ($CDCl_3$) and its cation **2′e** ($CDCl_3/CF_3COOD$, 7:3).

The molar ratio **2e**/CF_3COOH used for the NMR measurements was approximately 1:200. The ^{13}C NMR chemical shifts change slightly with a smaller excess of acid (1:100). The equilibrium **2e** + CF_3COOD ⇄ **2′e** + H_2O is not responsible for this result because we found an equivalent effect for model compound **7a**, which does not contain an OH group. We assume that the acid concentration is important for solvation complexes formed between the hexyloxy groups of **2e** or **7a** and CF_3COOD.

The treatment of the carbinols **2a**–**c** with CF_3COOD proved to be much more complex. Scheme 3 summarizes the processes. Carbinol **2a** behaves like the model compound **2e**. Protonation leads directly to the methylium salt **2′a**, which then can be subjected to further stepwise protonations (*m* = 1–3) to give **2′′′a**. In contrast, carbinols **2b**,**c** are first protonated on the amino groups to give the *N*-protonated carbinols **2′′b**,**c** before the *N*-protonated methylium ions **2′′′b**,**c** are generated. Accordingly, the unprotonated methylium salts **2′b** and **2′c** are not accessible. As the following discussion reveals, these results were obtained by studying the protonation by ^1H and ^{13}C NMR as well as by UV/Vis/NIR spectroscopy.

Figure 3 shows that all the ^1H NMR chemical shifts of **2a** are strongly downfield shifted for **2′′′a**, which exists in a high excess of acid ($CDCl_3/CF_3COOD$, 7:3). The greatest shift difference, $\Delta\delta$ = 0.93 ppm, is observed for the aromatic protons in the position *ortho* to the dialkylamino group. The highest $\Delta\delta(^1H)$ values for **2e** → **2′e** were observed for



Scheme 3. Protonation of the carbinols **2a**–**c**,**e**,**f**.

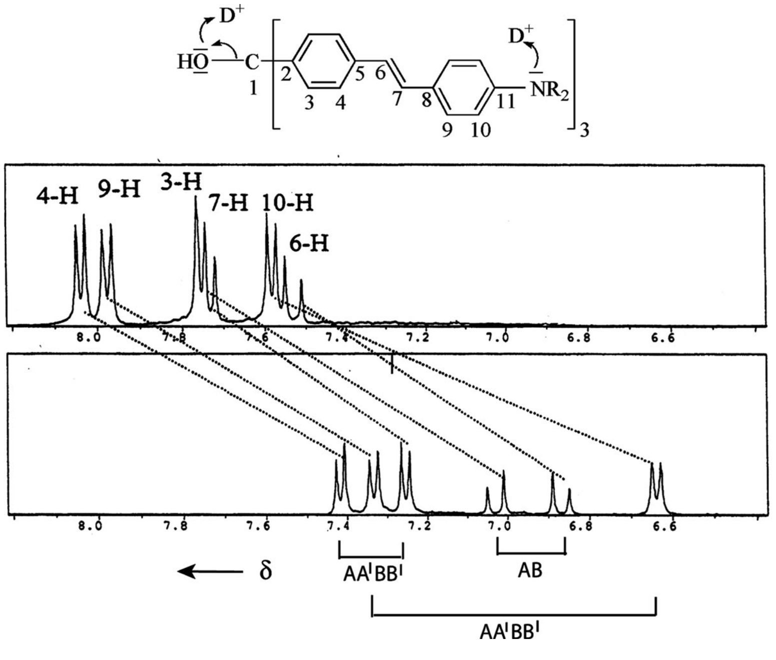


Figure 3. Low-field region of the ^{1}H NMR spectrum of **2a** in $CDCl_3$ (bottom) and of **2‴a** in $CDCl_3/CF_3COOD$ (7:3) (top). (The numbering does not correspond to the nomenclature.).

positions that are close to the central methylium carbon atom (Figure 2).

The ^{13}C NMR spectrum of **2‴a** indicates the formation of a delocalized methylium ion as the signal of the central carbon atom in **2a** is shifted from δ = 83.5 ppm in $CDCl_3$ to 198.2 ppm in $CDCl_3/CF_3COOD$ (7:3). Moreover, the excess acid protonates/deuteriates the dialkyamino groups. The *N*-CH_2 groups show a signal shift from δ = 57.2 to 66.2 ppm and the carbon atoms *ortho* to the dialkylamino group shift from δ = 113.4 to 122.6 ppm. The sizes of the $\Delta\delta$ values indicate that the major component in the strongly acidic medium is the tetracation **2‴** (m = 3).[15] An equilibrium with the trication **2′′′a** (m = 2) as a minor component cannot be completely excluded. The de facto C_{3h} symmetry is preserved in both cases.[16]

N-Protonation weakens and finally cancels the push–pull character of the methylium dyes AD$_3$. Thus, the crucial question was: can the ratio **2a**–**c**/CF$_3$COOD be so assessed that the tris(OPV)methylium dyes **2′a**–**c** are present without *N*-protonation? An NMR study of the equilibria **2′** ⇄ **2′′′** (m = 1) ⇄ **2′′′** (m = 2) ⇄ **2′′′** (m = 3) proved to be very difficult. Owing to the exchange processes many signals become very broad and can finally disappear in the electronic noise.[17] However, because UV/Vis/NIR absorption operates on a much faster timescale than NMR spectroscopy, absorption measurements were used to study the equilibria.

Compound **2a** in CH$_2$Cl$_2$ or CHCl$_3$ exhibits a long-wavelength band (Figure 4, a) with a maximum at 375 nm (ε = 84590 L mol^{-1}cm^{-1}). Slowly increasing the protonation (1.2×10^{-5} M **2a** and 1.2×10^{-5} to 2.2×10^{-4} M CF$_3$COOH) leads to the disappearance of this band, the formation of a few low-intensity bands in the region between 300 and 565 nm, and a strong NIR band at 1100 nm (Figure 4, a). Further increases in the CF$_3$COOH concentration in CH$_2$Cl$_2$ cause a steady decrease and a continuous blueshift of the maximum to 1050 nm. The solution used for the NMR measurements, which has a molar ratio for **2a**/CF$_3$COOD of 1:200, does not show any NIR absorption at all. Concomitant to the decrease in the NIR band, a new intense band with λ_{max} = 622 nm increases (Figure 4).

We assume that the NIR band corresponds to the equilibrium **2′a** ⇄ **2′′′a** (m = 1) with **2′a** as the major component (λ_{max} = 1100 nm). The chromophore of **2′a** contains three donor arms, which are cross-conjugated through the central acceptor to an AD$_3$ system. Figure 5 shows the immonium resonance structure of such an OPV arm. Only the cross-conjugated third arm has lost its donor character in **2′′′a** (m = 1) and therefore its electron transition should be only slightly higher in energy ($\lambda_{max} \approx$ 1050 nm) than that of **2′a**. A high excess of CF$_3$COOH/D certainly leads to **2′′′a** (m = 3) being the major component in the equilibrium **2′′′a** (m = 2) ⇄ **2′′′a** (m = 3). Therefore we conclude that the band with λ_{max} = 622 nm corresponds to this state, which has already been described above in the analysis of the ^{1}H and ^{13}C NMR spectroscopic data.

The carbinols **2b** (λ_{max} = 411 nm, ε = 155500 L mol cm^{-1}) and **2c** (λ_{max} = 419 nm, ε = 277200 L mol cm^{-1}) show on protonation a behavior that is quite different from that of **2a** and **2e**. The long-wavelength band is first blueshifted from 411 to 360 nm and from 419 to 370 nm, respectively. Further protonation decreases the intensity of the blueshifted band and generates a new band at the Vis/NIR border at λ_{max} = 732 (n = 2) and 783 nm (n = 3). We attribute the blueshifted band to the protonated carbinols **2′′b**,**c** and the finally generated band at the Vis/NIR border to the *N*-protonated methylium salts **2′′′b**,**c** (Scheme 3). Compounds **2′′b**,**c** (m = 1) should give, on further careful protonation, a methylium ion **2′′′b**,**c** (m = 1) with $\lambda_{max} \geq$ 1050 nm. We could not find such a species. Therefore we assume that the carbinols **2b**,**c** are two- or three-fold protonated before the methylium ions are formed [**2b**,**c** → **2′′b**,**c** (m = 2,3) → **2′′′b**,**c** (m = 2,3)]. Figure 4 (b) illustrates the protonation of **2c** (n = 3) and the characteristic difference in the protonation of **2a** (n = 1) shown in Figure 4 (a).

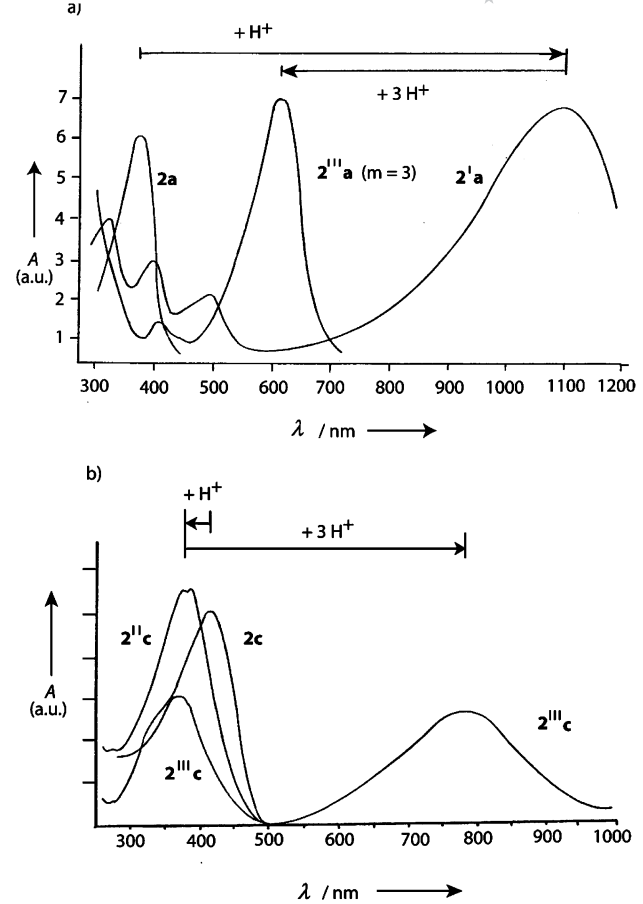
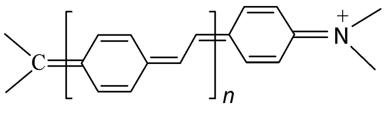


Figure 4. a) UV/Vis/NIR absorption of **2a** in CHCl$_3$, with **2′a** as the major component obtained by primary protonation and **2′′′a** (m = 3) obtained as the major component in the final protonation (CHCl$_3$/CF$_3$COOH). b) UV/Vis/NIR absorption of **2c** in CHCl$_3$, *N*-protonated carbinol **2′′c**, and methylium salt **2′′′c** (m = 3) as the major component after the final protonation with CF$_3$COOH (molar ratio **2c**/CF$_3$COOH, 1:200).



2′a n = 1

2′′′a-c n = 1–3
(m = 1, 2)

Figure 5. Immonium resonance structure of an unprotonated arm of **2′** and **2′′′**.

The exact λ_{max} values of **2′′′a**–**c** depend to some extent on the excess of CF$_3$COOH. Although a 200-fold molar excess of acid should favor **2′′′** (m = 3), **2′′′** (m = 2) as the minor component cannot be excluded. A strict distinction between m = 2 and m = 3 on the basis of a small variation in λ_{max} is not possible because we also observed such an effect for the alkoxy-substituted ions **2′e**. We assume that the solvation of the ions or better of the ion pairs in $CHCl_3$/CF_3COOH depends on the concentration of the acid. A related solvation effect is discussed above for the NMR measurements of the electroneutral compound **7c** in $CDCl_3$/CF_3COOD.

Figure 6 gives an overview of the absorption maxima of **2a–c**, **2′a**, and **2′′′a–c** and compares them with the hexyloxy-substituted carbinols **8a–d** (n = 1–4) and their methylium ions **8′a–d**.[7]

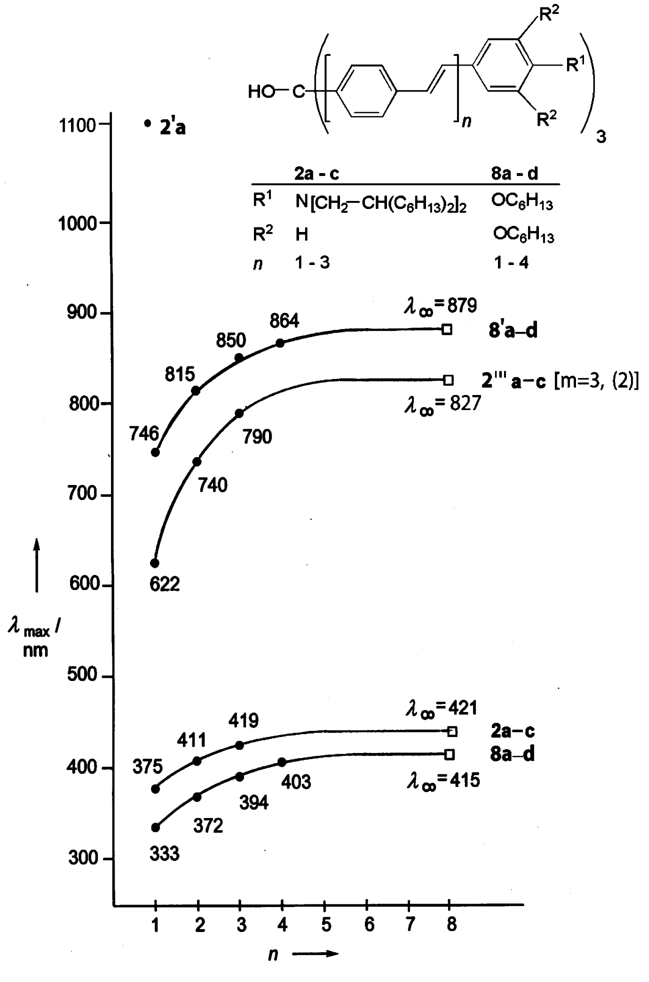


Figure 6. Absorption maxima of the carbinols **2a–c** and **8a–d** in $CHCl_3$, the methylium dyes **2a′** and **8′a–d**, and the protonated methylium dyes **2′′′a–c** in $CHCl_3$/CF_3COOH (7:3).

The carbinol series **2a–c** and **8a–d** are typical bathochromic series, which means their λ_{max} values are monotonously redshifted with increasing numbers n of repeat units and approach limiting values λ_∞ in accord with an empirical exponential function.[14,18] Recently, semiempirical and theoretically based algorithms were suggested for such convergence problems.[19–21] Formation of the methylium salts causes a redshift that in series **8′a–d** is even more pronounced than in **2′′′a–c** and leads to a convergence limit of λ_∞ at 879 nm. Compared with the carbinol series **2a–c** and **8a–d**, **2′′′a–c** and **8′a–d** have an extended conjugation, but only compounds **8′a–d** have a push–pull effect of the type AD_3. Consequently, the λ_{max} values of **2′′′** are, for each value of n, lower than the λ_{max} values of **8′**. The unprotonated series **2a–c** has, in contrast, for each value of n, higher λ_{max} values than **8a–c** because dialkylamino groups are stronger donors than alkoxy groups.

In the light of these results, the tris(aminostilbenyl)methylium salts with λ_{max} values of 952[12] and 1003 nm[11] published by Sengupta and Sadhukhan seem to be correct, whereas the systems reported by Steele[9] and Screttas and Nunzi[8] and their co-workers, which have λ_{max} values of 833 and 608 nm, respectively, are certainly polycations.

Stability

The tris(OPV)methylium dyes can be isolated in the solid state as tetrafluoroborates. The dark-blue salts are highly hygroscopic, hydrolyze rapidly (NMR control) in air or in aqueous solvents and start to fade. The carbinols **2a–f** are thermally but not photochemically stable. Cross-linking by the formation of C–C single bonds is a typical photoreaction of stilbenoid compounds.[13] In particular, energy-rich UV light, for example, λ_{irr} = 254 nm, leads to processes in which the conjugated chromophores are slowly destroyed. Stereoisomerization reactions (E) ⇄ (Z) are restricted to stilbenes. Higher-conjugated stilbenoid systems do not show this type of reaction because the bond order of the olefinic double bonds is not sufficiently reduced in the excitation of the ground state S_o to the first excited singlet state S_1.[13] Therefore compound **2a** (n = 1) is by far the most photosensitive compound in the series **2a–d**. The model system **2e** behaves in the same way. Figure 7 demonstrates the photoreactivity of **2e** for monochromatic irradiation with λ_{irr} = 366 nm. The long-wavelength band (λ_{max} = 330 nm in THF) is reduced and a new maximum at about 280 nm is generated. The process looks clean because an isosbestic point at λ = 274 is apparent. However, a ^1H NMR study of the probe after irradiation for 3 h revealed the presence of small amounts of cross-linked oligomers, even for irradiations at 366 nm. The major components during the entire irradiation are the original system (E,E,E)-**2e** and its (E,E,Z) and (E,Z,Z) isomers. For steric reasons only traces

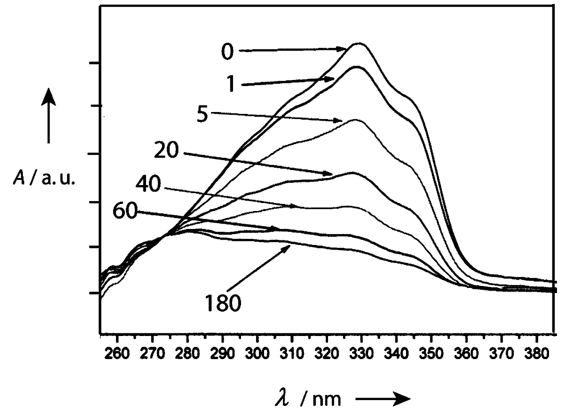
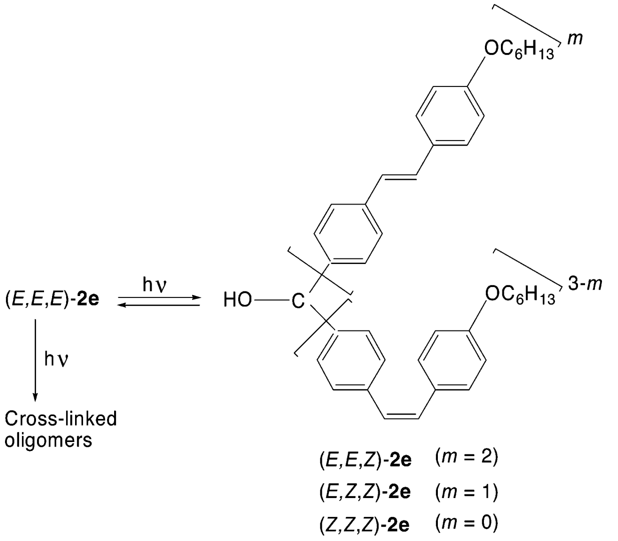


Figure 7. Reaction spectra of (E,E,E)-**2e** in THF after 0, 1, 5, 20, 40, 60, and 180 min of monochromatic irradiation (λ_{irr} = 366 nm).

of (*Z*,*Z*,*Z*)-**2e** can be formed and detected (Scheme 4). The (*Z*)-configured arms can be easily identified in the mixture by their olefinic AB systems in the ^{1}H NMR spectra, which are shifted from δ = 7.0–7.1 (^3J = 16 Hz) to 6.4–6.6 ppm (^3J = 10 Hz). The structures of the generated oligomers were not studied.



Scheme 4. Photoreactions of **2e**.

Conclusion and Outlook

Carbinols **2a**–**f** with three OPV arms can be prepared by the Wittig–Horner reaction and simultaneous autoxidation. Compounds **2a**–**d** with terminal dialkylamino groups exhibit unexpected protonation behavior. The lowest member **2a** (n = 1) first forms by *O*-protonation and elimination of water the corresponding methylium salt **2′a** before *N*-protonation to **2′′′a** occurs. The higher members **2b**,**c** (n = 2,3) are first *N*-protonated to the carbinols **2′′b**,**c** before the *N*-protonated methylium ions **2′′′b**,**c** are generated. This distinction has a big effect on the long-wavelength electron transition. The methylium ion **2′a** is a push–pull system AD_3 with an absorption far into the NIR region (λ_{max} = 1100 nm),[22] whereas the tetracations **2′′′a**–**c** have absorption maxima in the visible region (λ_{max} = 622, 740, and 790 nm). They represent a bathochromic series [$\lambda(n+1) \geq \lambda(n)$] for which a convergence limit at λ_∞ = 827 nm can be predicted. The star-shaped molecules **2**, **2′**, and **2′′′** promise as nanoparticles[23,24] interesting SHG and TPA properties, although their photostability is limited when they are irradiated with UV light.

Experimental Section

General Remarks: UV/Vis: Zeiss MCS 320/340. ^{1}H and ^{13}C NMR: Bruker AMX 400, Avance 600, $CDCl_3$ as solvent, unless otherwise stated; TMS as internal standard. MS (FD): Finnigan MAT 95. Melting points: Büchi apparatus and Stuart Scientific SMP/3; uncorrected. Elemental analyses: Microanalytical laboratory of the Institute of Organic Chemistry, University of Mainz.

General Procedure for Preparation of the Carbinols 2a–f: Triphosphonate **3**[7] (69.5 mg, 0.10 mmol) and aldehyde **4a**–**d**,[25] **4e**,[26] or **4f**[27,28] (0.40 mmol) dissolved in dry THF (20 mL) were dropped into a solution of $KOC(CH_3)_3$ (2.25 g, 20.0 mmol) in THF (40 mL). The mixture was stirred at ambient temperature for 3–4 d and then poured onto crushed ice (50 g). The extract (40 mL CH_2Cl_2) was dried ($MgSO_4$) and the solvents evaporated. The crude products **2a**, **2b**, and **2e** were purified by filtration through silica gel (10 × 13 cm, toluene/$CHCl_3$ gradient from 100:0 to 80:20). The products **2c**, **2d**, and **2f** were precipitated by the addition of ethanol or methanol to the extract.

***all*-(*E*)-Tris[4-(2-{4-[bis(2-hexyloctyl)amino]phenyl}vinyl)phenyl]-methanol (2a):** Yield 122 mg (68%); yellow, viscous oil. ^{1}H NMR (CD_2Cl_2): δ = 0.89 (m, 36 H, CH_3), 1.16–1.33 (m, 120 H, CH_2), 1.78–1.88 (m, 6 H, CH), 3.25 (d, ^3J = 6.3 Hz, 12 H, NCH_2), 6.65/7.35 (AA′BB′, 12 H, arom. H, outer benzene rings), 6.88/7.04 (AB, ^3J = 16.2 Hz, 6 H, olefin. H), 7.27/7.43 (AA′BB′, 12 H, arom. H, inner benzene rings) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 23.1, 27.0, 30.2, 30.3, 32.2, 32.4 (CH_2, partly superimposed), 36.2 (CH), 57.2 (NCH_2), 82.2 (COH), 113.4, 125.9, 128.0, 128.7 (arom. CH), 123.4, 129.8 (olefin. CH), 125.0, 138.0, 145.9, 149.0 (arom. C_q) ppm. MS (FD): *m/z* (%) = 1790 (100) $[M]^{+\cdot}$. UV ($CHCl_3$): λ_{max} = 375 nm, ε = 84590 L mol^{-1} cm^{-1}. $C_{127}H_{205}N_3O$ (1790.1): calcd. C 85.22, H 11.54, N 2.35; found C 85.20, H 11.25, N 2.33.

***all*-(*E*)-Tris(4{2-[4-(2-{4-[bis(2-hexyloctyl)amino]phenyl}vinyl)phenyl]vinyl}phenyl)methanol (2b):** Yield 101 mg (48%); yellow solid, m.p. 55 °C. ^{1}H NMR ($CDCl_3$): δ = 0.87 (m, 36 H, CH_3), 1.17–1.34 (m, 120 H, CH_2), 1.78–1.88 (m, 6 H, CH), 3.21 (d, ^3J = 6.3 Hz, 12 H, NCH_2), 6.63/7.36 (AA′BB′, 12 H, arom. H, outer benzene rings), 6.87/7.04 (AB, ^3J = 16.2 Hz, 6 H, olefin. H, outer double bonds), 7.09 (′′s′′, 6 H, olefin. H, inner double bonds), 7.30/7.47 (AA′BB′, 12 H, arom. H, inner benzene rings), 7.43–7.47 (m, 12 H, arom. H, middle benzene rings) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6, 26.4, 29.7, 31.7, 31.8 (CH_2, partly superimposed), 35.5 (CH), 57.2 (NCH_2), 81.7 (COH), 113.5, 126.0, 126.2, 126.8, 127.3, 128.2 (arom. CH), 123.6, 127.3, 128.9, 128.9 (olefin. CH), 125.9, 135.6, 136.6, 137.9, 145.9, 145.9 (arom. C_q) ppm. MS (FD): *m/z* (%) = 2096 (100) $[M]^{+\cdot}$. UV/Vis ($CHCl_3$): λ_{max} = 411 nm, ε = 155500 L mol^{-1} cm^{-1}. $C_{151}H_{223}N_3O$ (2096.5): calcd. C 86.51, H 10.72, N 2.00; found C 86.49, H 10.70, N 1.89.

***all*-(*E*)-Tris{4-[2-(4-{2-[4-(2-{4-[bis(2-hexyloctyl)amino]phenyl}-vinyl)phenyl]vinyl}phenyl)vinyl]phenyl}methanol (2c):** Yield 108 mg (45%); orange solid, m.p. 175 °C. ^{1}H NMR ($CDCl_3$): δ = 0.87 (m, 36 H, CH_3), 1.17–1.33 (m, 120 H, CH_2), 1.81–1.90 (m, 6 H, CH), 3.24 (d, ^3J = 6.4 Hz, 12 H, NCH_2), 6.65/7.37 (AA′BB′, 12 H, arom. H, outer benzene rings), 6.87/7.07 (AB, ^3J = 16.3 Hz, 6 H, olefin. H, outer double bonds), 7.13–7.19 (m, 9 H, olefin. H), 7.29–7.57 (m, 39 H, arom. and olefin. H) ppm. ^{13}C NMR (CD_3SOCD_3): δ = 14.3 (CH_3), 23.1, 26.8, 30.1, 31.9, 32.2 (CH_2, partly superimposed) 35.9 (CH), 57.0 (NCH_2), 81.9 (COH), 113.0, 126.5, 126.5, 127.1, 127.2, 127.2, 127.9, 128.6 (arom. CH), 123.1, 127.6, 128.1, 128.7, 128.9, 129.4 (olefin. CH), 124.5, 135.9, 136.8, 136.8, 137.4, 138.3, 146.5, 148.6 (arom. C_q) ppm. MS (FD): *m/z* (%) = 2403 (3) $[M]^{+\cdot}$, 794 (19), 793 (49), 792 (100). UV/Vis ($CHCl_3$): λ_{max} = 419 nm, ε = 277200 L mol^{-1} cm^{-1}. $C_{175}H_{241}N_3O$ (2402.9): calcd. C 87.48, H 10.11, N 1.75; found C 87.34, H 10.14, N 1.72.

***all*-(*E*)-Tris[4-(2-{4-[2-(4-{2-[4-(2-{4-[bis(2-hexyloctyl)amino]phenyl}vinyl)phenyl]vinyl}phenyl)vinyl]phenyl}vinyl)phenyl]methanol (2d):** Yield 22 mg (8%); red-orange solid, m.p. >230 °C (decomp.). ^{1}H NMR ([D$_8$]THF): δ = 0.79 (m, 36 H, CH_3), 1.14–1.27 (m, 120 H, CH_2), 1.73–1.81 (m, 6 H, CH), 3.18 (d, ^3J = 6.5 Hz, 12 H, NCH_2), 6.58/7.39 (AA′BB′, 12 H, arom. H, outer benzene rings), 6.81/6.98

(AB, ^3J = 16.4 Hz, 6 H, olefin. H, outer double bonds), 7.06/7.09 (AB, ^3J = 16.4 Hz, 6 H, olefin. H), 7.05–7.12 (m, 6 H, olefin. H), 7.20–7.47 (m, 54 H, arom. and olefin. H) ppm. ^{13}C NMR ([D$_8$]-THF): δ = 14.4 (CH$_3$), 23.5, 27.3, 30.7, 32.4, 32.7 (CH$_2$, partly superimposed), 36.5 (CH), 57.4 (NCH$_2$), 81.5 (COH), 113.7, 123.9, 125.9, 126.5, 126.8, 127.4, 128.1, 128.3, 128.7, 128.9, 129.1, 129.2, 129.7 (olefin. and arom. CH, partly superimposed), 125.9, 136.6, 137.0, 137.6, 137.7, 137.8, 138.0, 138.8, 148.3, 148.9 (arom. C$_q$) ppm. MS (FD): m/z (%) = 2709 (3) [M]$^{+\cdot}$, 1815 (6), 998 (26), 895 (100). Owing to the low yield, further characterizations and studies of the compound have been omitted.

***all*-(*E*)-Tris(4-{2-[4-(hexyloxy)phenyl]vinyl}phenyl)methanol (2e):** Yield 61 mg (70%); almost colorless solid, m.p. 115 °C. ^{1}H NMR (CDCl$_3$): δ = 0.91 (t, 6 H, CH$_3$), 1.30–1.40 (m, 12 H, CH$_2$), 1.41–1.53 (m, 6 H, CH$_2$), 1.75–1.85 (m, 6 H, CH$_2$), 3.95 (t, ^3J = 6.6 Hz, 6 H, OCH$_2$), 6.84/7.39 (AA′BB′, 12 H, arom. H, outer benzene rings), 6.92/7.02 (AB, ^3J = 16.4 Hz, 6 H, olefin. H), 7.18/7.31 (AA′BB′, 12 H, arom. H, inner benzene rings) ppm. ^{13}C NMR (CDCl$_3$): δ = 14.0 (CH$_3$), 22.6, 25.7, 29.3, 31.6 (CH$_2$), 68.2 (OCH$_2$), 81.8 (COH), 114.8, 125.9, 127.8, 128.3 (arom. CH), 126.0, 128.7 (olefin. CH), 130.0, 136.8, 145.7, 159.0 (arom. C$_q$) ppm. MS (FD): m/z (%) = 866 (100) [M]$^{+\cdot}$. $C_{61}H_{70}O_4$ (867.2): calcd. C 84.48, H 8.14; found C 84.39, H 8.11.

***all*-(*E*)-Tris(4-{2-[3,4-bis(hexyloxy)phenyl]vinyl}phenyl)methanol (2f):** Yield 76 mg (65%); almost colorless solid, m.p. 109 °C. ^{1}H NMR (CDCl$_3$): δ = 0.89 (m, 18 H, CH$_3$), 1.31–1.36 (m, 24 H, CH$_2$), 1.44–1.48 (m, 12 H, CH$_2$), 1.77–1.86 (m, 12 H, CH$_2$), 3.99 (t, 6 H, OCH$_2$), 4.03 (t, 6 H, OCH$_2$), 6.84/7.00/7.05 (ABC, 9 H, arom. H, outer benzene rings), 6.93/7.02 (AB, ^3J = 16.1 Hz, 6 H, olefin. H), 7.27/7.42 (AA′BB′, 10 H, arom. H, inner benzene rings) ppm. ^{13}C NMR (CDCl$_3$): δ = 14.0 (CH$_3$), 22.6, 22.6, 31.6, 31.6, 25.7, 25.8, 29.3, 29.4 (CH$_2$), 69.5, 69.6 (OCH$_2$), 81.8 (COH), 112.0, 114.1, 120.1 (arom. CH, outer benzene rings), 125.9, 128.2 (arom. CH, inner benzene rings), 126.2, 129.0 (olefin. CH), 130.6, 136.8, 145.8, 149.4, 149.5 (arom. C$_q$) ppm. MS (FD): m/z (%) = 1167 (100) [M]$^{+\cdot}$. $C_{79}H_{106}O_7$ (1167.7): calcd. C 81.26, H 9.15; found C 81.08, H 9.07.

***all*-(*E*)-Tris(4-{2-[4-(hexyloxy)phenyl]vinyl}phenyl)methane (7a):** Ethyl tris(p-tolyl)methyl ether (**5**)[6,29] and Schiff base **6a**[28] were prepared according to the literature. A mixture of KOC(CH$_3$)$_3$ (3.37 g, 30.0 mmol) and **6a** (5.63 g, 20.0 mmol) in dry DMF (100 mL) was degassed and purged with Ar before **5** (1.0 g, 3.0 mmol) in DMF (30 mL) was slowly added. After 1 h vigorous stirring at 80 °C, the mixture was poured onto crushed ice (300 g) and treated with 6 M HCl (100 mL, 600 mmol) for about 1 h. Extraction with CHCl$_3$ (3 × 50 mL) gave an organic phase that was washed with water (2 × 50 mL), dried (Na$_2$SO$_4$), and the solvents evaporated. The residue was recrystallized from ethanol. Yield 1.66 g (65%); colorless crystals, m.p. 121–122 °C. ^{1}H NMR (CDCl$_3$): δ = 0.89 (t, 9 H, CH$_3$), 1.31–1.34 (m, 12 H, CH$_2$), 1.42–1.46 (m, 6 H, CH$_2$), 1.73–1.78 (m, 6 H, CH$_2$), 3.95 (t, 6 H, OCH$_2$), 5.51 (s, 1 H, CH), 6.86/7.40 (AA′BB′, 12 H, arom. H, outer benzene rings), 6.89/7.02 (AB, ^3J = 16.0 Hz, 6 H, olefin. H), 7.09/7.40 (AA′BB′, 12 H, arom. H, inner benzene rings) ppm. ^{13}C NMR (CDCl$_3$): δ = 14.0 (CH$_3$), 22.6, 25.7, 29.3, 31.6 (CH$_2$), 56.2 (CH), 68.2 (OCH$_2$), 114.8, 126.3, 127.7, 129.8 (arom. CH), 126.2, 128.2 (olefin. CH), 130.1, 136.0, 143.0, 159.0 (arom. C$_q$) ppm. MS (FD): m/z (%) = 851 (100) [M + H]$^+$. $C_{61}H_{70}O_3$ (851.2): calcd. C 86.07, H 8.29; found C 85.99, H 8.35.

***all*-(*E*)-Tris(4-{2-[4-(dodecyloxy)phenyl]vinyl}phenyl)methane (7b):** The procedure applied for **7a** was also used for the preparation of **7b**. Ether **5**[6](1.0 g, 3.0 mmol) and Schiff base **6b**[26] (7.31 g, 20 mmol) gave 2.15 g (65%) of **7b**. The colorless crystals melted after recrystallization from ethanol at 132 °C. ^{1}H NMR (CDCl$_3$): δ = 0.87 (t, 9 H, CH$_3$), 1.23–1.36 (m, 48 H, CH$_2$), 1.42–1.47 (m, 6 H, CH$_2$), 1.73–1.79 (m, 6 H, CH$_2$), 3.95 (t, 6 H, OCH$_2$), 5.51 (s, 1 H, CH), 6.86/7.39 (AA′BB′, 12 H, arom. H, outer benzene rings), 6.93/7.02 (AB, ^3J = 16.3 Hz, 6 H, olefin. H), 7.10/7.39 (AA′BB′, 12 H, arom. H, inner benzene rings) ppm. ^{13}C NMR (CDCl$_3$): δ = 14.1 (CH$_3$), 22.7, 25.9, 29.2, 29.3, 29.5, 29.6, 31.9 (CH$_2$, partly superimposed), 56.2 (CH), 68.2 (OCH$_2$), 114.8, 126.0, 126.3, 127.7, 128.2, 129.7 (arom. and olefin. CH), 130.1, 136.0, 142.9, 159.0 (arom. C$_q$) ppm. MS (FD): m/z (%) = 1104 (100) [M + H]$^+$. $C_{79}H_{106}O_3$ (1103.7): calcd. C 85.97, H 9.68; found C 85.92, H 9.35.

Generation of the Methylium Trifluoroacetates 2′a, 2′e, and 2′′′a–c: Carbinol **2a** (36 mg, 0.02 mmol) was dissolved in CH$_2$Cl$_2$ or CHCl$_3$ (1–2 mL) and treated with trifluoroacetic acid (10–40 mg, 0.1–0.4 mmol). The spontaneous formation of **2′a** as the major component in the equilibrium **2a** ⇄ **2′a** ⇄ **2′′′a** (m = 1) was evident by the color change from light-yellow to blue. The polycations **2′′′a–c** (m = 3) ⇄ **2′′′a–c** (m = 2) were obtained when **2a–c** (0.02 mmol) were dissolved in 7:3 mixtures of CHCl$_3$/CF$_3$COOH or CH$_2$Cl$_2$/CF$_3$COOH (1 mL). The molar ratio **2a–c**/CF$_3$COOH amounts in these cases to 1:200. The latter procedure was also performed for the generation of **2′e**.

***all*-(*E*)-Tris[4-(2-{4-[bis(2-hexyloctyl)ammonium]phenyl}vinyl)-phenyl]methylium Tetra(trifluoroacetate) (2′′′a):** ^{1}H NMR (CDCl$_3$/CF$_3$COOD, 7:3): δ = 0.86–0.95 (m, 36 H, CH$_3$), 1.20–1.47 (m, 120 H, CH$_2$), 1.55–1.64 (m, 6 H, CH), 3.60–3.68 (m, 12 H, NCH$_2$), 7.53/7.75 (AB, ^3J = 16.5 Hz, 6 H, olefin. H), 7.58/7.98 (AA′BB′, 12 H, arom. H, outer benzene rings), 7.76/8.04 (AA′BB′, 12 H, arom. H, inner benzene rings) ppm. ^{13}C NMR (CDCl$_3$/ CF$_3$COOD 7:3): δ = 13.7 (CH$_3$), 22.8, 26.2, 29.5, 31.4, 31.9 (CH$_2$, partly superimposed), 34.7 (CH), 66.2 (NCH$_2$), 122.6, 129.0, 130.7, 142.0 (arom. CH), 130.6, 135.8 (olefin. CH), 137.9, 139.9, 140.0, 150.6 (arom. C$_q$), 198.2 (central C) ppm. Vis/NIR: $\lambda_{\max}$ = 622 nm (CHCl$_3$/CF$_3$COOH = 7:3).

***all*-(*E*)-Tris(4-{2-[4-(2-{4-[bis(2-hexyloctyl)ammonium]phenyl}vinyl)-phenyl]vinyl}phenyl)methylium Tetra(trifluoroacetate) (2′′′b):** ^{1}H NMR (CDCl$_3$/CF$_3$COOD, 7:3): δ = 0.86–0.94 (m, 36 H, CH$_3$), 1.22–1.50 (m, 120 H, CH$_2$), 1.58–1.66 (m, 6 H, CH), 3.58–3.70 (m, 12 H, NCH$_2$), 7.36/7.44 (AB, ^3J = 16.5 Hz, 6 H, olefin. H), 7.40–7.54 (m, 9 H, arom. and olefin. H), 7.72–7.85 (m, 21 H, arom. and olefin. H), 7.89–7.94 (m, 6 H, arom. H), 8.01–8.06 (m, 6 H, arom. H) ppm. ^{13}C NMR (CDCl$_3$/CF$_3$COOD, 7:3): δ = 13.8 (CH$_3$), 23.0, 26.5, 29.7, 31.9, 32.1 (CH$_2$), 34.8 (CH), 66.4 (NCH$_2$), 122.2, 127.6, 128.3, 128.7, 129.3, 129.8, 129.9, 132.8, 136.0, 139.1, 139.5, 141.6, 142.0 (arom. and olefin. CH and C$_q$, partly superimposed), 198.0 (central C) ppm. Vis/NIR: $\lambda_{\max}$ = 740 nm (CHCl$_3$/CF$_3$COOH = 7:3).

***all*-(*E*)-Tris{4-[2-(4-{2-[4-(2-{4-[bis(2-hexyloctyl)ammonium]phenyl}vinyl)phenyl]vinyl}phenyl)vinyl]phenyl}methylium Tetra(trifluoroacetate) (2′′′c):** Vis/NIR: $\lambda_{\max}$ = 790 nm (CHCl$_3$/CF$_3$COOH = 7:3). The ^{1}H and ^{13}C NMR spectra exhibit broad overlapping signals.

***all*-(*E*)-Tris(4-{2-[4-(hexyloxy)phenyl]vinyl}phenyl)methylium Trifluoroacetate (2′e):** ^{1}H NMR (CDCl$_3$/CF$_3$COOD, 7:3): δ = 0.88–0.94 (m, 9 H, CH$_3$), 1.33–1.40 (m, 12 H, CH$_2$), 1.44–1.53 (m, 6 H, CH$_2$), 1.81–1.90 (m, 6 H, CH$_2$), 4.14–4.21 (m, 6 H, OCH$_2$), 7.06/7.66 (AA′BB′, 12 H, arom. H, outer benzene rings), 7.25/7.66 (AB, ^3J = 16.1 Hz, 6 H, olefin. H), 7.66/7.89 (AA′BB′, 12 H, inner benzene rings) ppm. ^{13}C NMR (CDCl$_3$/CF$_3$COOD, 7:3): δ = 13.1 (CH$_3$), 22.2, 25.2, 28.7, 31.3 (CH$_2$), 69.7 (OCH$_2$), 116.0, 127.6, 129.8, 140.3 (arom. CH), 124.5, 138.1 (olefin. CH), 138.8, 150.9, 160.4, 191.0 (arom. C_q) ppm.

Isolation of the Dyes in the Solid State: The carbinols **2a**–**c**,**e** (0.02 mmol) were dissolved in CH_2Cl_2 (10 mL) and treated with HBF_4 (2 mL) and acetic anhydride (2 mL). The salts **2′e** and **2′′′a**–**c** precipitated as dark-blue solids and were purified by evaporation of the volatile parts at 10^2 Pa. They are highly hygroscopic, attract water, become sticky and start to fade.

Irradiation of Carbinol 2e: A solution of (*E*,*E*,*E*)-**2e** (9 mg, 0.01 mmol) was irradiated in THF/[D_8]THF (1 mL). (A saturated solution of **2e** in CH_2Cl_2/CD_2Cl_2 can be used as well.) An Osram XBO-1000 W OFR lamp in an AMKO device was used. The monochromator was adjusted to 366 nm, which is on the long-wavelength end of the absorption. Thus, photocrosslinking could be kept to a minimum. The isomerization process (Scheme 4) was followed by UV and ^{1}H NMR measurements. Compound **2a** was treated in a similar way.

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[15] The protonation/deuteriation of *N*,*N*-diethylaniline in $CDCl_3/CF_3COOD$ (7:3) serves here as an equivalent model. The $\Delta\delta$ values found for the CH_2 groups and the *ortho* carbon atoms for **2a**→**2′′′a** amount to about 90% of the $\Delta\delta$ values obtained for diethyl(phenyl)ammonium trifluoroacetate. This value is a clear indication that the tetracation **2′′′a** ($m = 3$) is a major component.

[16] Owing to the fast intra- and intermolecular proton exchange, mediated by the trifluoroacetate anions, the trications **2′′′a** ($m = 2$) also have C_{3h} symmetry.

[17] Another drawback is the H/D exchange at the position *ortho* to the dialkylamino group.

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[22] The extended conjugation of the AD_3 system causes such an enormous bathochromic shift in comparison with tris(4-dimethylaminophenyl)methylium ions (Crystal Violet: λ_{max} = 590 nm).

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[29] NMR spectroscopic data for **5**. ^{1}H NMR ($CDCl_3$): δ = 1.26 (t, 3 H, CH_3), 2.35 (s, 9 H, CH_3), 3.14 (q, 2 H, OCH_3), 7.13/7.37 (AA′BB′, 12 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.4 (CH_3 of OC_2H_5), 21.1 (CH_3), 59.3 (OCH_2), 86.1 (CO), 128.5, 128.5 (arom. CH), 136.3, 142.0 (arom. C_q) ppm.

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