Synthesis of Tetrastilbenylmethanes by Wittig−Horner Reactions

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The all-(*E*)-configured tetrastilbenylmethanes **3a**–**e** and **5a**,**b** can be obtained by fourfold Wittig–Horner reactions. The tetrahedral arrangement of these compounds guarantees independent stilbenoid chromophores with a high chromophore density. Apart from (*E*)/(*Z*) isomerization reactions, irradiation leads to a three-dimensional network with isolated unchanged stilbene units.

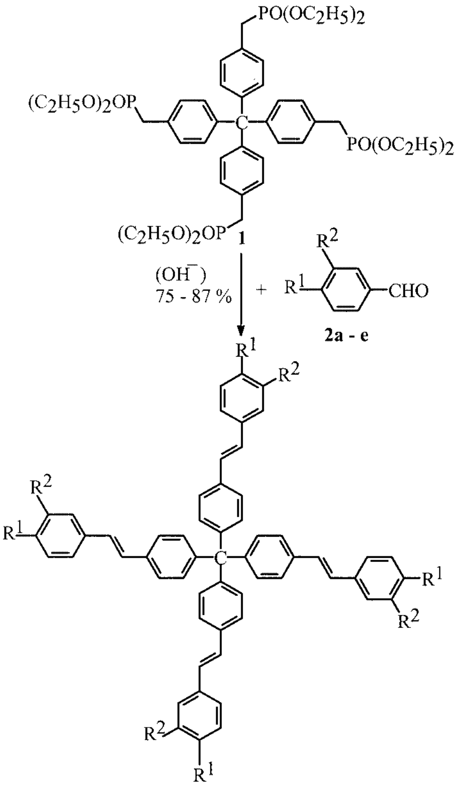
Introduction

Stilbenoid chromophores attract a great deal of attention in materials science because of their interesting properties.[1] For many applications, a high density of the chromophores as well as the formation of amorphous films with a low crystallization tendency is important. Linear and planar stilbenoid compounds tend to aggregate due to π stacking (and possibly due to the interactions of solubilizing side chains). Therefore, a tetrahedral arrangement seems to be appropriate. Moreover, such a geometry is suitable for the photochemical generation of a three-dimensional network.

Results and Discussion

In the context of the generation of a tetrakis(squaraine), we recently prepared the fourfold phosphonate **1**,[2] which proved to be suitable for the synthesis of the tetrastilbenylmethanes **3a**−**e** (Scheme 1). The Wittig−Horner reactions of **1** and the aldehydes **2a**−**e** give the target compounds in good yields and with very high *trans* stereoselectivities. Until now, the few known tetrastilbenylmethanes were prepared by applying the Heck reaction[3,4] or a modified Heck reaction via fourfold diazonium salts.[5]

The conjugated "arms" were extended by a similar procedure, however, the yields of the reactions of **1** and the aldehydes **4a**,**b** (Scheme 2) were somewhat lower. All the C−C double bonds of **5a**,**b** were shown to have the *trans* configuration by ^{1}H NMR spectroscopy, whereby the limit of detection of a *cis* isomer was below 5%. The alkoxy chains in **5a**,**b** as well as in **3a**−**d** enhance the solubility of these compounds and also lower their HOMO−LUMO gaps (bandgaps). The latter effect is even stronger in **3e** which contains a *para*-dimethylamino group.



3	a	b	c	d	e
R^1	OC_6H_{13}	$OC_{12}H_{25}$	OC_6H_{13}	$OC_{12}H_{25}$	$N(CH_3)_2$
R^2	H	H	OC_6H_{13}	$OC_{12}H_{25}$	H
[%] Yield	87	78	80	83	75

Scheme 1. Preparation of the tetrastilbenylmethanes **3a**−**e** by Wittig−Horner reactions

The ^{1}H NMR spectroscopic data of the products **3a**−**e** and **5a**,**b** are listed in Table 1; the most characteristic ^{13}C NMR signals were found for the central carbon atoms (δ = 64.3 ± 0.1 ppm) and the adjacent carbon atoms of the inner benzene rings (δ = 145.8 ± 0.4 ppm). These signals are

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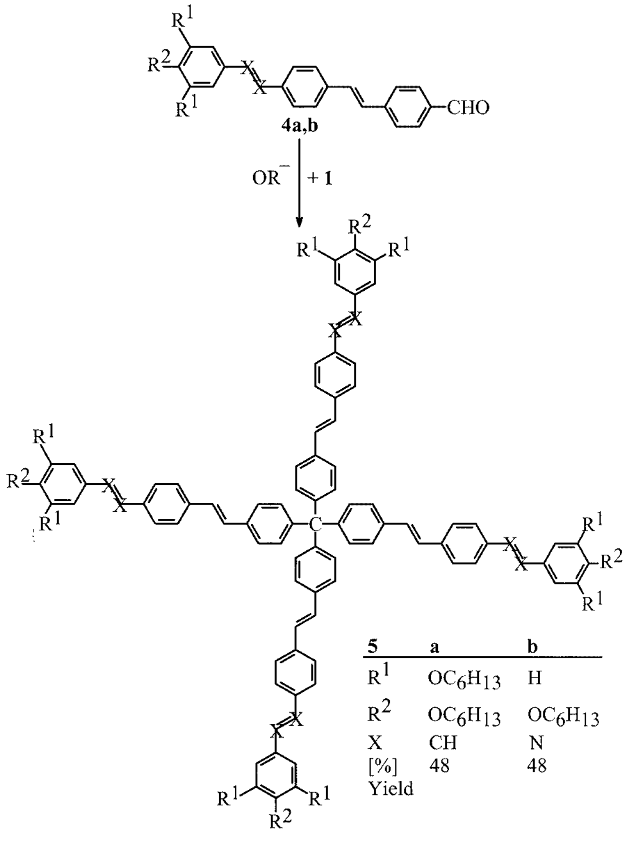

5	a	b
R^1	OC_6H_{13}	H
R^2	OC_6H_{13}	OC_6H_{13}
X	CH	N
[%] Yield	48	48

Scheme 2. Preparation of the four-arm compounds **5a**,**b** with extended chromophores

typical for tetraphenylmethane cores.[6] The other ^{13}C chemical shifts are described in the Exp. Sect.

The UV absorption spectra of the four alkoxy-substituted compounds **3a**−**d** are very similar; the maxima $\lambda_{max.}$ of the long-wavelength band are at 336 ± 3 nm, and have very high intensities (log $\varepsilon = 5.09 \pm 0.02$). The dimethylamino group in **3e** causes a red-shift to $\lambda_{max.} = 363$ nm (log $\varepsilon = 5.00$). The compounds with extended chromophores **5a** and **5b** exhibit strong absorptions at $\lambda_{max.} = 375$ nm (log $\varepsilon = 5.32$) and $\lambda_{max.} = 393$ nm (log $\varepsilon = 5.28$), respectively.

The interactions between the four "arms" are small. The long-wavelength absorption corresponds to the chromophores of equivalent (*E*)-stilbenes, (*E*,*E*)-1,4-distyrylbenzenes and (*E*,*E*)-4-styrylazobenzenes, respectively.[4,7,8] Therefore, a Förster-type incoherent energy transfer between the arms on a subpicosecond time scale can be assumed; such an effect was established for a closely related compound, namely tetrakis[4-(2-{4-[2-(3,5-di-*tert*-butylphenyl)vinyl]phenyl}vinyl)phenyl]methane.[7]

Apart from the photophysics, the photochemistry of the stilbenoid chromophores present in **3a**−**e** and **5a** is expected to be interesting. Figure 1 (top) illustrates the monochromatic ($\lambda = 366$ nm) irradiation of **3a**. The initial curve ($t = 0$) corresponds to the all-(*E*) configuration, which is first transformed to the mono-*cis* form; the maximum at $\lambda = 330$ nm disappears and a shoulder (sh) at 310 nm becomes evident. The ^1H NMR spectrum of the latter reveals the generation of the *cis* isomer by a new AB spin pattern at $\delta = 6.46/6.52$ ppm with $^3J = 11.6$ Hz. Continued irradiation at 366 nm transforms more and more *trans*-configured arms into *cis* arrangements: (*E*,*E*,*E*,*E*) → (*E*,*E*,*E*,*Z*) → (*E*,*E*,*Z*,*Z*); the steric congestion around the central carbon atom is so severe that an all-(*Z*) isomer and even a mono-*trans* isomer seem to be unlikely. During irradiation at 366 nm, the light is selectively absorbed by the *trans*-configured arms; therefore, a photostationary state is avoided under these conditions. Prolonged monochromatic irradiation ($t > 60$ min) or, better, irradiation with a Pyrex filter ($\lambda \geq 290$ nm) leads to a new situation shown in the lower part of Figure 1. Novel maxima appeared at 270 and 290 nm. This region is characteristic of the absorptions of 1,4-dialkyl- and 1-alkoxy-4-alkylbenzenes. ^1H NMR measurement revealed at this stage a broad signal of tertiary CH protons at $\delta = 4.4$ ppm. From many other stilbenoid compounds, it is well known that C−C bond formation of the olefinic centers can occur.[1b] Since the olefinic double bonds within a molecule of **3a** are too far away from each other for an intramolecular reaction, intermolecular processes must take place exclusively. Thus, a three-dimensional network of benzene with isolated stilbene chromophores (Figure 1) was generated. The solubility of the product decreased and finally we obtained a polymer.[9]

Table 1. ^1H NMR spectroscopic data for **3a**−**c** and **5a**,**b** measured in $CDCl_3$

Comp.	Benzene rings inner AA'BB'	middle AA'BB'	outer AA'MM' ABM or A_2	Olefinic Protons AB	^3J [Hz]	OCH_2 t or 2 t	CH_2 m	CH_3 t or 2 t
3a	7.20, 7.32		6.83, 7.38	6.90, 6.98	16.3	3.94	1.30 – 1.42, 1.74	0.89
3b	7.23, 7.37		6.86, 7.41	6.93, 7.02	16.4	3.95	1.26 – 1.44, 1.77	0.88
3c	7.22, 7.37		6.82, 6.99 7.04	6.90, 7.00	16.3	3.99 4.03	1.31 – 1.48, 1.82	0.89
3d	7.22, 7.37		6.82, 6.99 7.05	6.90, 7.00	16.3	3.99 4.03	1.24 – 1.47, 1.80	0.86
3e	7.22, 7.37		6.70, 7.37	6.88, 7.02	16.3			2.96 (s)
5a	7.26, 7.42	7.47 (s)	6.70	6.94, 7.06 7.08 (s)	16.2	3.96 4.01	1.32 – 1.48 1.74, 1.81	0.89
5b	7.37, 7.54	7.68, 7.89	7.02, 7.87	7.20, 7.31	16.1	4.02	1.32 – 1.48, 1.74	0.89

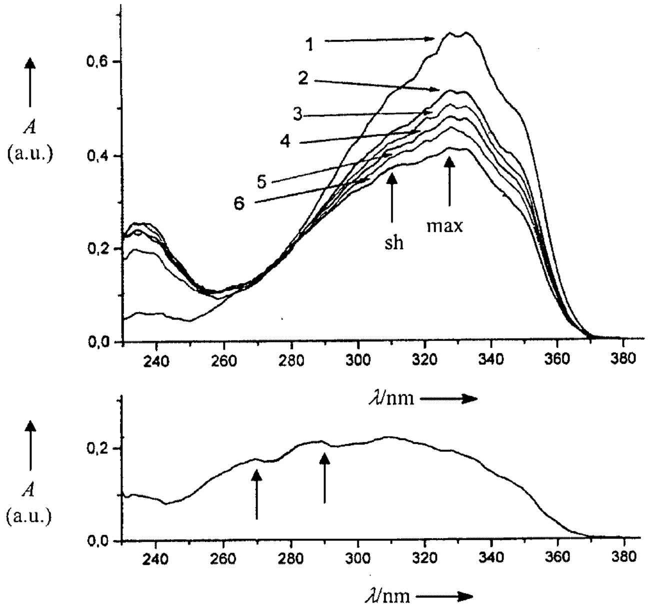

Figure 1. UV/Vis spectra (absorbance A versus wavelength λ) of the irradiation (366 nm) of **3a** in [D$_8$]THF; top: *trans/cis* isomerization; 1 (t = 0 min), 2 (5 min), 3 (15 min), 4 (25 min), 5 (35 min), 6 (45 min); bottom: the beginning of crosslinking by prolonged irradiation ($t \geq$ 1 h)

Whereas the photochemistry of compounds **3b−e** and **5a** is similar, the azobenzene system **5b** behaves differently. Irradiation with a long-wavelength band ($\lambda_{max.}$ = 393 nm) leads to selective photoisomerization at the N−N double bond in accord with our earlier study of 4,4′-distyrylazobenzenes.[8,10] The *cis*-configured azobenzene moieties then revert to the *trans* configurations thermally at ambient temperatures. We attribute the chemoselective isomerization of the N=N bond to a highly efficient *N*-inversion mechanism.[11] In contrast to azobenzene, the extended conjugation in **5b** leads to strong interactions between the $n\pi^*$ and $\pi\pi^*$ excited states which favors this process.[11] Prolonged irradiation again leads to photocrosslinking.

Conclusion

The tetrakis(stilbenyl)methanes **3a−e** and two compounds **5a**,**b** with extended conjugation in the four "arms" were prepared by applying fourfold Wittig−Horner reactions. The all-(*E*)-configured chromophores hardly interact in the tetrahedral arrangement. The absorption spectra and photochemistry of **3a−e**, **5a** and **5b** resemble the corresponding stilbenes, 1,4-distyrylbenzenes and 4-styrylazobenzenes, respectively. Irradiation leads primarily to *trans/cis* isomerization reactions, whereby in **5b** the azo substructure is exclusively involved. Prolonged irradiation of **3a** furnishes a three-dimensional network with isolated stilbene chromophores. The process is based on C−C bond formation between the original olefinic centers. Compounds **3b−e** and **5a** behave similarly.

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, and the IR spectra with a Beckman Acculab 4. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM 400 spectrometer with CDCl$_3$ as solvent unless otherwise noted, using TMS as the internal standard. The FD mass spectra were obtained with a Finnigan MAT 95 apparatus. Elemental analyses were performed in the microanalytical laboratory of the Institute of Organic Chemistry at the University of Mainz, Germany.

all-(*E*)-Tetrakis(4-{2-[4-(hexyloxy)phenyl]vinyl}phenyl)methane (3a): A suspension of KOH (100 mg, 1.78 mmol) in DMF (20 mL) was warmed to 60 °C in a flask, which was carefully flushed with Ar. 4-Hexyloxybenzaldehyde (**2a**) (1.12 g, 5.43 mmol) and diethyl 4-(tris-{4-[(diethoxyphosphoryl)methyl]phenyl}methyl)benzylphosphonate (**1**)[2] (1.0 g, 1.09 mmol) in DMF (20 mL) were added dropwise at 0 °C to the suspension. After 24 h at room temperature, crushed ice (100 g) was added. The mixture was extracted twice with CHCl$_3$ (50 mL each), the organic layer dried with MgSO$_4$ and the solvents were evaporated. The residue was recrystallized from ethanol. Yield 1.07 g (87%), m.p. 218 °C. UV (CHCl$_3$): $\lambda_{max.}$ = 339 nm, ε = 118595 cm^2·mmol^{-1}. ^{13}C NMR ([D$_8$]THF):[12] δ = 14.0 (CH$_3$), 22.6, 25.7, 29.2, 31.6 (CH$_2$), 64.4 (C$_q$, central C), 68.1 (OCH$_2$), 114.7, 125.4, 127.7, 131.3 (aromat. CH), 125.9, 128.3 (olefin. CH), 130.0, 135.3, 145.7, 158.8 (aromat. C$_q$) ppm. FD MS: *m/z* (%) = 1129 (100) [M$^+$]. C$_{81}$H$_{92}$O$_4$ (1129.6): calcd. C 86.13, H 8.21; found C 86.15, H 8.18.

all-(*E*)-Tetrakis(4-{2-[4-(dodecyloxy)phenyl]vinyl}phenyl)methane (3b): The preparation was performed according to the procedure described for **3a**. Recrystallization from ethanol yielded 78% of **3b** (1.25 g from 1.0 g **1**) as colorless crystals, m.p. 176 °C. UV (CHCl$_3$): $\lambda_{max.}$ = 339 nm, ε = 118595 cm^2·mmol^{-1}. ^{13}C NMR (CDCl$_3$):[12] δ = 14.1 (CH$_3$), 22.7, 26.0, 29.3, 29.3, 29.4, 29.5, 29.6, 29.6, 29.6, 31.9 (CH$_2$, superimposed), 64.4 (C$_q$, central C), 68.1 (OCH$_2$), 114.8, 125.5, 127.7, 131.3 (aromat. CH), 126.0, 128.3 (olefin. CH), 130.1, 135.4, 145.7, 158.9 (aromat. C$_q$) ppm. FD MS: *m/z* (%) = 1467 (100) [M + H$^+$]. C$_{105}$H$_{140}$O$_4$ (1466.3): calcd. C 86.01, H 9.62; found C 85.79, H 9.63.

all-(*E*)-Tetrakis(4-{2-[3,4-bis(hexyloxy)phenyl]vinyl}phenyl)methane (3c): The preparation was performed according to the procedure described for **3a**. Aldehyde **2c**[13] and **1**[2] yielded 80% of **3c** (1.33 g from 1.0 g **1**) as colorless crystals, m.p. 90 °C (CHCl$_3$/C$_2$H$_5$OH). UV (CHCl$_3$): $\lambda_{max.}$ = 339 nm, ε = 116487 cm^2·mmol^{-1}. ^{13}C NMR (CDCl$_3$):[12] δ = 14.0 (CH$_3$), 22.6−31.6 (CH$_2$, superimposed), 64.3 (C$_q$, central C), 69.3, 69.4 (OCH$_2$), 112.0, 114.1, 120.0, 125.5, 131.3 (aromat. CH), 126.2, 128.7 (olefin. CH), 130.7, 135.3, 145.8, 149.3, 149.4 (aromat. C$_q$) ppm. FD MS: *m/z* (%) = 1531 (100) [M + H$^+$]. C$_{105}$H$_{140}$O$_8$ (1530.3): calcd. C 82.41, H 9.22; found C 82.37, H 9.16.

all-(*E*)-Tetrakis(4-{2-[3,4-bis(dodecyloxy)phenyl]vinyl}phenyl)methane (3d): The preparation was performed according to the procedure described for **3a**. Aldehyde **2d**[14] and **1** yielded 83% of **3d** (1.99 g from 1.0 g **1**) as colorless crystals, m.p. 75 °C (CHCl$_3$/C$_2$H$_5$OH). UV (CHCl$_3$): $\lambda_{max.}$ = 337 nm, ε = 128395 cm^2·mmol^{-1}. ^{13}C NMR (CDCl$_3$):[12] δ = 14.0 (CH$_3$), 22.6−31.9 (CH$_2$, superimposed), 64.4 (C$_q$, central C), 69.4, 69.5 (OCH$_2$), 112.0, 114.1, 120.0, 125.5, 131.3 (aromat. CH), 126.2, 128.7 (olefin. CH), 130.7, 135.3, 145.8, 149.3, 149.4 (aromat. C$_q$) ppm. FD MS: *m/z* (%) = 2203 (100) [M$^+$]. C$_{153}$H$_{236}$O$_8$ (2203.6): calcd. C 83.40, H 10.80; found C 83.37, H 10.78.

all-(*E*)-Tetrakis(4-{2-[4-(dimethylamino)phenyl]vinyl}phenyl)-methane (3e): The preparation was performed according to the procedure described for **3a**. Yield 75% (0.737 g from 1.0 g **1**), m.p. 298 °C ($CHCl_3/CH_3OH$). UV ($CHCl_3$): $\lambda_{max.}$ = 363 nm, ε = 100348 $cm^2 \cdot mmol^{-1}$. ^{13}C NMR ($CDCl_3$):[12] δ = 40.4 (NCH_3), 64.2 (C_q, central C), 112.5, 125.1, 127.5, 131.3 (aromat. CH), 124.1, 128.7 (olefin. CH), 126.1, 135.8, 145.4, 150.1 (aromat. C_q) ppm. FD MS: *m*/*z* (%) = 901 (100) [M^+]. $C_{65}H_{64}N_4$ (901.3): calcd. C 86.63, H 7.16, N 6.22; found C 86.36, H 6.98, N 6.02.

all-(*E*)-Tetrakis{4-[2-(4-{2-[3,4,5-tris(hexyloxy)phenyl]vinyl}-phenyl)vinyl]phenyl}methane (5a): The preparation was performed according to the procedure described for **3a**, but the reaction time at room temperature was extended to 48 h. Aldehyde **4a**[15] and **1**[2] yielded 45% of **5a** (1.15 g from 1.0 g **1**) as yellow crystals, m.p. 130 °C, obtained from a solution of $CHCl_3$ to which C_2H_5OH was slowly added. UV ($CHCl_3$): $\lambda_{max.}$ = 375 nm, ε = 207024 $cm^2 \cdot mmol^{-1}$. ^{13}C NMR ($CDCl_3$):[12] δ = 14.0, 14.0 (CH_3), 22.6, 22.7, 25.8, 25.8, 29.5, 30.3, 31.6, 31.8 (CH_2), 64.4 (C_q, central C), 69.4, 73.6 (OCH_2), 105.6, 125.8, 126.7, 126.8, 131.3 (aromat. CH), 127.3, 128.0, 128.5, 128.8 (olefin. CH), 132.6, 135.2, 136.6, 136.9, 138.7, 146.1, 153.4 (aromat. C_q). FD MS: *m*/*z* (%) = 2339 (100) [$M + H^+$]. $C_{161}H_{212}O_{12}$ (2339.5): calcd. C 82.66, H 9.13; found C 82.63, H 9.14.

(*E*,*E*)-4-[2-(4-{2-[4-(Hexyloxy)phenyl]diazenyl}phenyl)vinyl]-benzaldehyde (4b): A mixture of (*E*)-4-[2-(4-hydroxyphenyl)diazenyl]benzaldehyde (4.71 g, 20.8 mmol),[16] 1-bromohexane (8.25 g, 49.9 mmol), K_2CO_3 (6.25 g, 45.2 mmol) and KI (17 mg, 0.1 mmol) in dry dioxane (150 mL) was refluxed for 24 h. The hot solution was filtered and cooled to 5 °C. The precipitate formed was recrystallized twice from $(CH_3)_2CHOH$. Small red crystals were obtained (1.94 g, 30%) which melted at 83 °C. ^1H NMR ($CDCl_3$): δ = 0.90 (t, 3 H, CH_3), 1.28−1.48 (m, 6 H, CH_2), 1.85 (m, 2 H, CH_2), 4.03 (t, 2 H, OCH_2), 6.98 (AA′ part of AA′MM′, 2 H, aromat. H), 7.92 (MM′, 2 H, aromat. H), 7.95−8.00 (AA′BB′, 4 H, aromat. H), 10.06 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6, 25.7, 29.1, 31.6 (CH_2), 68.5 (OCH_2), 114.9, 123.0, 125.4, 130.7 (aromat. CH), 136.9, 146.9, 156.2, 162.6 (aromat. C_q), 191.6 (CHO) ppm. FD MS: *m*/*z* (%) = 310 (100) [M^+]. $C_{19}H_{22}N_2O_2$ (310.4): calcd. C 73.52, H 7.14, N 9.03; found C 73.19, H 7.00, N 9.33.

all-(*E*)-Tetrakis{4-[2-(4-{2-[4-(hexyloxy)phenyl]diazenyl}phenyl)-vinyl]phenyl}methane (5b): A suspension of $KOC(CH_3)_3$ (2.00 g, 18.0 mmol) in dry THF (30 mL) was carefully flushed with Ar. Tetraphosphonate **1** (1.0 g, 1.09 mmol) and aldehyde **4b** (2.76 g, 5.43 mmol) in dry THF (30 mL) were added dropwise at 0 °C to the suspension. After stirring at room temperature for 48 h, the workup was carried out as described for **3a**. Yield 1.22 g (48%), m.p. 130 °C ($CHCl_3/C_2H_5OH$).[12] UV ($CHCl_3$): $\lambda_{max.}$ = 393 nm, ε = 190000 $cm^2 \cdot mmol^{-1}$. IR (KBr): $\tilde{\nu}$ = 2920, 2850, 1570, 1500, 1460, 1425, 1370, 1340, 1310, 1230, 1110, 1020, 960, 830, 720, 620 cm^{-1}. FD MS: *m*/*z* (%) = 1547 (100) [$M + H^+$]. $C_{105}H_{108}N_8O_4$ (1546.1): calcd. C 81.57, H 7.04, N 7.25; found C 81.85, H 7.09, N 7.23.

Irradiation Experiments: The monochromatic irradiations were performed in [D_8]THF with an AMKO high-pressure xenon lamp and an interference filter (λ = 366 nm). A Hanovia 450 W mercury middle-pressure lamp with Pyrex filter ($\lambda \geq$ 290 nm) served for the photoreactions, which were investigated by ^1H NMR spectroscopy.

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