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Polyalkynylanthracenes – syntheses, structures and their behaviour towards UV irradiation†

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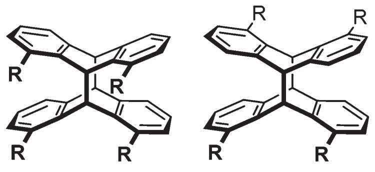
A series of bis- and tris[(trimethylsilyl)ethynyl]anthracenes (1,5-, 1,8-, 9,10- and 1,8,10-) has been synthesised by multistep (cross coupling) reactions and the behaviour of the $SiMe_3$-functionalised alkynylanthracene derivatives towards UV irradiation was qualitatively studied by NMR spectroscopy. In the case of 9,10-bis[(trimethylsilyl)ethynyl]anthracene we observed a photodimerisation upon UV irradiation; the third example was reported for a symmetrically 9,10-difunctionalised anthracene derivative, besides those with small fluorine- and methyl-substituents. The anthracene dimerisation is completely thermally reversible and the temperature dependence of the cycloelimination reaction was studied by ^{1}H VT-NMR experiments. The (deprotected) 1,5- and 1,8-diethynylanthracenes were converted with (dimethylamino)-trimethylstannane to obtain the corresponding $SnMe_3$-functionalised alkynes, potentially useful as highly conjugated building blocks in Stille cross coupling reactions. The new anthracene compounds were completely characterised by multinuclear NMR spectroscopy, (high resolution) mass spectrometry and – in most cases – by X-ray diffraction experiments.

Introduction

Anthracenes and their substituted derivatives undergo cycloaddition reactions upon irradiation with UV light.[1] In the case of functionalised anthracenes like 1,8-substituted ones, a mixture of the so-called *head to head*- (**A**) and *head to tail*- (**B**) photodimers is obtained (Scheme 1). Owing to steric interactions of the substituents, the *head to tail* isomer is the preferred product in most cases.[2]

(Di-) substituted anthracenes find various applications as photoswitchable units, *e.g.* in supramolecular systems,[3] as their photodimerisation reactions are mostly found to be similar to unsubstituted anthracene, *i.e.* [4 + 4] cycloaddition leading to the 9,10:9′,10′ photodimer.[4] However, other types of (mono-) substituted anthracene dimerisations, called *non-classical photodimers*, have been observed, *e.g.* in the case of 9-(phenylethynyl)anthracene ([4 + 2] cycloaddition) or *trans*-1-(9-anthryl)-2-phenylethylene ([6 + 6] cycloaddition).[1b,5]



A **B**

Scheme 1 Photodimerisation products of 1,8-substituted anthracene derivatives.

Due to steric repulsion of the substituents, the photodimerisation of 9,10-disubstituted anthracenes is rarely explored. Nevertheless, some examples are known. Some unsymmetrically substituted anthracene derivatives have been found to undergo photodimerisation yielding [4 + 4] cycloaddition products, which are thermally labile in most cases.[1b] Until now, symmetrically 9,10-disubstituted anthracenes are known to be difficult to dimerise, except for 9,10-difluoro-[6] and 9,10-dimethylanthracene.[7]

Results and discussion

Syntheses and characterisation of the anthracene derivatives

The bis[(trimethylsilyl)ethynyl]-functionalised anthracenes **3**, **4** and **10** were obtained by Kumada and Sonogashira-Hagihara cross coupling reactions using 1,5- (**1**) and 1,8-dichloroanthracene (**2**) as well as 9,10-dibromoanthracene (**9**), respectively (Scheme 2).[8,9] After cleaving the $SiMe_3$ groups, the deprotected dialkynes **5** and **6** were converted with (dimethylamino)trimethylstannane and the $SnMe_3$-functionalised compounds **7**

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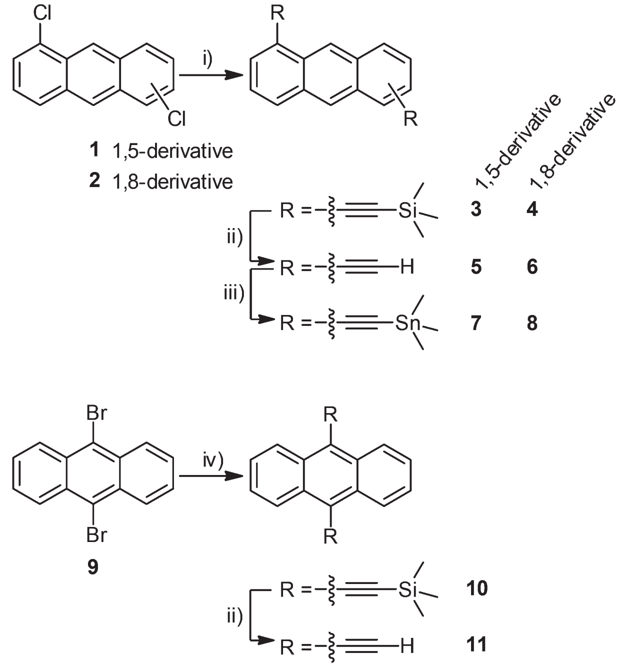


Scheme 2 Syntheses of the 1,5-, 1,8- and 9,10-dialkynylsubstituted anthracene derivatives. Reagents and conditions: (i) 1. $Me_3SiC{\equiv}CMgBr$ (7 eq.), Ni(acac)$_2$, PPh_3, THF, reflux; 2. aq. workup, 82% (**3**), 92% (**4**); (ii) K_2CO_3, MeOH, r.t., 93% (**5**), 82% (**6**), 25% (**11**); (iii) Me_3SnNMe_2, THF, 60 °C, 4 h, quant. (**7** and **8**); (iv) 1. $Me_3SiC{\equiv}CH$ (2 eq.), CuI (10 mol%), $PdCl_2(PPh_3)_2$ (5 mol%), (i-Pr)$_2$NH, reflux, 3 d; 2. aq. workup, 38%.

and **8** were obtained in quantitative yield. These terminally $SnMe_3$-functionalised dialkynyl anthracenes might be applicable as highly conjugated (photoswitchable) building blocks, *e.g.* when two functionalities should be linked by Stille cross coupling reactions.[10] All compounds were characterised by multinuclear NMR spectroscopy as well as (high resolution) mass spectrometry. Tables 1 and 2 provide the ^1H NMR spectroscopic shifts of the 1,5- and 1,8-substituted derivatives for comparison.

Table 1 ^1H NMR shifts of the 1,5-dialkynylsubstituted compounds **3** (E = Si), **5** and **7** (E = Sn) in $CDCl_3$ (500 MHz, 298 K). For NMR spectroscopic assignments see Scheme 7

	H9/H10	H4/H8	H2/H6	H3/H7	C≡C–H	$E(CH_3)_3$
3	8.88	8.06	7.74	7.44	—	0.39
5	8.93	8.10	7.79	7.46	3.60	—
7	8.93	8.04	7.72	7.42	—	0.48

Table 2 ^1H NMR shifts of the 1,8-dialkynylsubstituted compounds **4** (E = Si), **6** and **8** (E = Sn) in $CDCl_3$ (500 MHz, 298 K). For NMR spectroscopic assignments see Scheme 7

	H9	H10	H4/H5	H2/H7	H3/H6	C≡C–H	$E(CH_3)_3$
4	9.32	8.42	7.98	7.79	7.42	—	0.39
6	9.44	8.45	8.03	7.80	7.45	3.62	—
8	9.43	8.40	8.95	7.76	7.40	—	0.46

We also tried to convert 9,10-diethynylanthracene (**11**) into the corresponding $SnMe_3$ substituted species. However, the brownish product was found to be insoluble in common organic solvents and could not be analysed so far.

The molecular structures in the crystalline state of compounds **3**, **4**, **5**, **7** and **8** are displayed in Fig. 1–4 (the structure of **6** was previously published by us[11]). They were determined

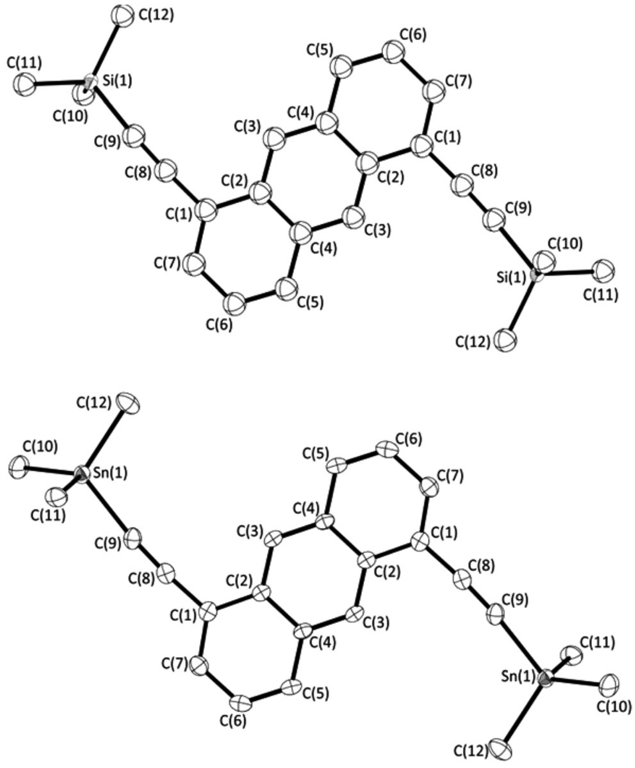


Fig. 1 Molecular structures of compounds **3** (above) and **7** (below) in the crystalline state. Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths and angles are listed in Table 3.

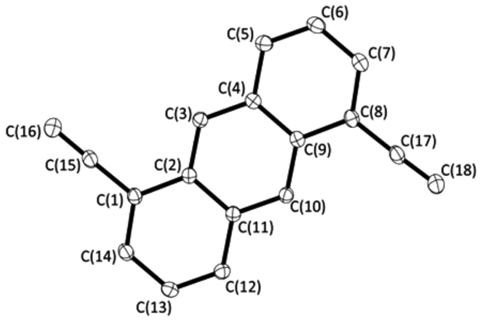


Fig. 2 Molecular structure of compound **5** in the crystalline state. Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.445(1), C(1)–C(14) 1.378(1), C(1)–C(15) 1.435(1), C(2)–C(3) 1.396(1), C(2)–C(11) 1.436(1), C(15)–C(16) 1.195(1); C(1)–C(2)–C(3) 122.3(1), C(1)–C(2)–C(11) 118.4(1), C(1)–C(15)–C(16) 178.5(1), C(2)–C(1)–C(14) 120.2(1), C(2)–C(1)–C(15) 119.5(1).

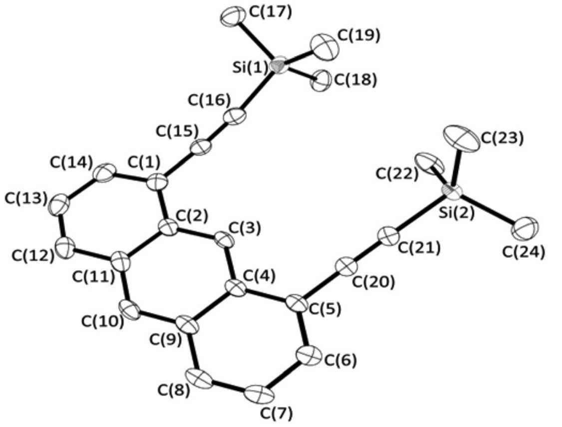


Fig. 3 Molecular structure of compound **4** in the crystalline state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted and only one molecule is shown for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.443(2), C(1)–C(14) 1.377(2), C(1)–C(15) 1.440(2), C(2)–C(3) 1.396(2), C(2)–C(11) 1.438(2), C(5)–C(20) 1.437(2), C(6)–C(7) 1.416(2), C(16)–Si(1) 1.842(1), C(17)–Si(1) 1.864(2); C(1)–C(2)–C(3) 122.6(1), C(1)–C(2)–C(11) 118.3(1), C(1)–C(15)–C(16) 176.0(1), C(2)–C(1)–C(15) 120.5(1), C(5)–C(20)–C(21) 178.5(1), C(15)–C(16)–Si(1) 173.9(1), C(20)–C(21)–Si(2) 177.1(1).

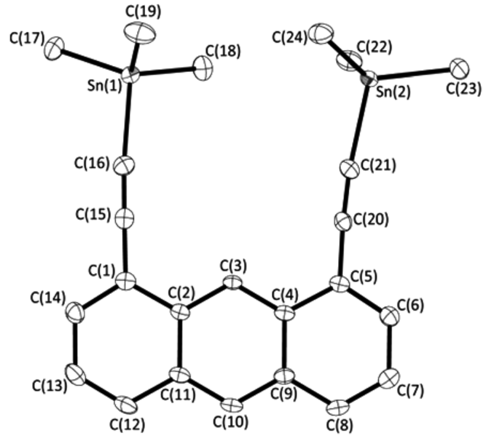


Fig. 4 Molecular structure of compound **8** in the crystalline state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted and only one molecule is shown for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.448(2), C(1)–C(14) 1.381(2), C(1)–C(15) 1.431(3), C(2)–C(3) 1.400(2), C(2)–C(11) 1.430(2), C(5)–C(20) 1.433(3), C(6)–C(7) 1.415(3), C(16)–Sn(1) 2.114(2), C(17)–Sn(1) 2.127(2); C(1)–C(2)–C(3) 122.1(2), C(1)–C(2)–C(11) 118.6(2), C(1)–C(15)–C(16) 177.5(2), C(2)–C(1)–C(15) 120.1(2), C(5)–C(20)–C(21) 176.0(2), C(15)–C(16)–Sn(1) 171.5(2), C(20)–C(21)–Sn(2) 174.7(2).

Table 3 Selected bond lengths [Å] and angles [°] of compounds **3** and **7**

	3 (E = Si)	**7** (E = Sn)
C(1)–C(2)	1.447(1)	1.452(3)
C(1)–C(7)	1.376(1)	1.380(3)
C(1)–C(8)	1.437(1)	1.434(3)
C(2)–C(3)	1.397(1)	1.393(3)
C(2)–C(4)	1.436(1)	1.433(3)
C(8)–C(9)	1.209(2)	1.210(3)
C(9)–E(1)	1.844(1)	2.113(2)
C(10)–E(1)	1.866(1)	2.131(2)
C(1)–C(2)–C(3)	122.4(1)	122.4(2)
C(1)–C(2)–C(4)	118.5(1)	118.6(2)
C(1)–C(8)–C(9)	175.5(1)	175.2(2)
C(2)–C(1)–C(7)	120.0(1)	119.7(2)
C(2)–C(1)–C(8)	119.1(1)	118.6(2)
C(8)–C(9)–E(1)	171.9(1)	166.2(2)

by X-ray diffraction experiments of single crystals grown from solutions by slow evaporation of the solvent (see the Experimental section for details). Due to the fact that similar structural parameter values are observed for compounds **3** and **7**, as well as for compounds **4** and **8**, their molecular structures are described together.

The terminally $SiMe_3$- and $SnMe_3$-substituted 1,5-diethynylanthracenes **3** and **7** exhibit inversion centres in the middle of their central anthracene rings. The aromatic systems are planar with C–C distances ranging from 1.367(2) Å [C(5)–C(6), **3**] and 1.364(3) Å [C(5)–C(6), **7**] to 1.447(1) Å [C(1)–C(2), **3**] and 1.452(3) Å [C(1)–C(2), **7**], respectively. The alkynyl substituents are nearly in the same plane as the anthracene backbone; this is manifest from the surrounding angles of C(1), which are close to 120° [maximum deviations are 0.9° (**3**) and 1.7° (**7**)]. The angles C(1)–C(8)–C(9) [175.5(2)° (**3**) and 175.2(2)° (**7**)] and C(8)–C(9)–E(1) [171.9(2)° (**3**) and 166.2(2)° (**7**)] show the (trimethylelement)ethynyl groups to be slightly bent out of linearity and they are found to be not in-plane with the anthracene units as is indicated in the dihedral angles C(6)–C(7)–C(1)–C(8) at 175.3(1)° (**3**) and 177.0(2)° (**7**), respectively. The silicon and tin atoms are tetrahedrally coordinated with E(1)–C_{Me} distances in the expected range.[12] The C≡C bond lengths of compounds **3** [1.209(2) Å] and **7** [1.210(3) Å] are identical within experimental error and with the standard triple bond length of 1.20 Å.[12]

The molecular structure of the deprotected 1,5-diethynylanthracene (**5**) depicted in Fig. 2 exhibits no unexpected bond lengths and angles. Carbon atoms C(1) and C(8) are trigonal-planar coordinated with the three surrounding angles being close to 120°. The alkynyl substituents are found to be in-plane with the planar anthracene skeleton. With "aromatic" C–C distances between 1.367(1) Å [C(5)–C(6)] and 1.436(1) Å [C(4)–C(9)], the structural parameters are well comparable with those of 1,8-diethynylanthracene (**6**).[11]

The $SiMe_3$-substituted 1,8-dialkynylanthracene **4** is depicted in Fig. 3 and the important structural parameters of both molecules are listed in Table 4.

After recrystallisation from *n*-hexane, the molecular structure of the $SnMe_3$ derivative **8** was also determined by X-ray diffraction experiments (Fig. 4). In contrast to the corresponding 1,5-substituted compound **7**, four molecules of 1,8-bis[(trimethylstannyl)ethynyl]anthracene (**8**) and one *n*-hexane molecule are found in the asymmetric unit. Selected value ranges of the corresponding bond lengths and angles of **4** and **8** are listed in Table 4 for comparison. A few remarkably different values were measured demonstrating the variability of structural parameters of independent molecules for the

Table 4 Selected value ranges (minimum and maximum) of bond lengths [Å] and angles [°] of compounds **4** and **8**

	4 (E = Si)		**8** (E = Sn)	
	min.	max.	min.	max.
C_{Ar}–C≡	1.437(2)	1.440(2)	1.427(3)	1.438(3)
–C≡C–	1.205(2)	1.209(2)	1.200(3)	1.210(3)
≡C–E	1.842(1)	1.847(1)	2.105(2)	2.123(2)
E–C_{Me}	1.849(2)	1.864(2)	2.126(2)	2.137(2)
C_{Ar}–C_{Ar}	1.356(2)	1.443(2)	1.355(3)	1.449(2)
C_{Ar}–C_{Ar}–C_{Ar}	117.9(1)	122.6(1)	118.0(2)	122.4(2)
C_{Ar}–C_{Ar}–C≡	118.9(1)	121.1(1)	119.2(2)	121.5(2)
C_{Ar}–C≡C	174.4(1)	178.5(1)	174.9(2)	179.6(2)
C≡C–E	173.9(1)	177.1(1)	170.2(2)	176.3(2)
≡C–E–C_{Me}	106.3(1)	109.4(1)	103.1(1)	109.0(1)
C_{Me}–E–C_{Me}	109.5(2)	112.1(1)	108.9(1)	117.7(1)

same compound, a fact that has also been observed in the X-ray diffraction results of 1,8-diethynylanthracene (**6**).[11] Nevertheless, the bond lengths and angles determined for compounds **4** and **8** are in the expected ranges and the values are comparable to those of the corresponding 1,5-substituted derivatives **3** and **7** described above in more details. Exact values for certain molecules are given in Fig. 3 and 4.

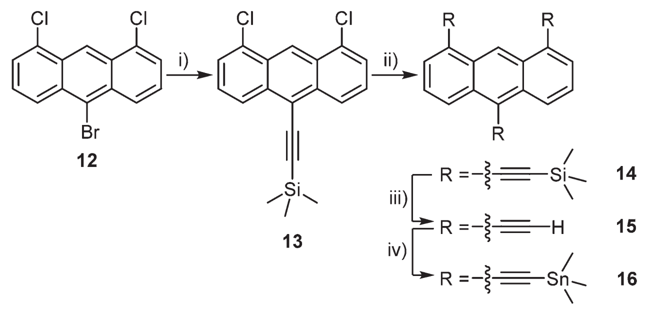
Starting from 10-bromo-1,8-dichloroanthracene (**12**),[13] the tris[(trimethylsilyl)ethynyl]-substituted species **14** was synthesised in a two-step reaction *via* 1,8-dichloro-10-[(trimethylsilyl)ethynyl]anthracene (**13**), as is displayed in Scheme 3. **13** can also be prepared (in lower yields) by conversion of 1,8-dichloroanthracene-10-(9*H*)-one with [(trimethylsilyl)ethynyl]-magnesium bromide in THF.[14] Deprotection of the alkynyl units of **14** led to the formation of **15** which was converted with (dimethylamino)trimethylstannane to afford 1,8,10-tris-[(trimethylstannyl)ethynyl]anthracene (**16**).

However, compared to the 1,5- and 1,8-disubstituted compounds **7** and **8**, the obtained product was found to be unstable towards air and moisture. Anyway, we found some evidence for the successful synthesis of the desired threefold $SnMe_3$-substituted compound **16** stemming from ^1H NMR data of the raw product. As expected for 1,8,10-trisubstituted anthracenes, the ^1H NMR spectrum recorded at ambient temperature (298 K) in $CDCl_3$ shows one downfield-shifted singlet at δ = 9.44 ppm (H9), two doublets at 8.58 ppm (H4/H5) and 7.78 ppm (H2/H7), as well as one doublet of doublets at 7.50 ppm (H3/H6). Two singlets at 0.49 ppm and 0.46 ppm (integral ratio 9 : 18) show typical ^{117}Sn- and ^{119}Sn-satellites, indicating the availability of two different trimethylstannyl groups.

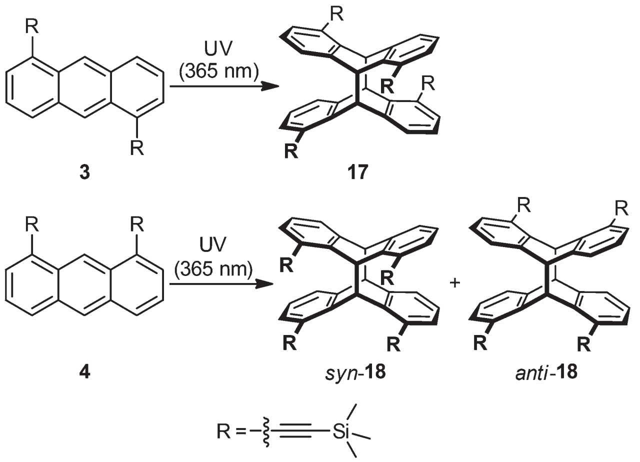
Photodimerisation reactions

To investigate the influence of the (trimethylsilyl)ethynyl substituent positions on the *syn–anti* ratio of the anthracene dimerisation, the corresponding compounds were irradiated with UV light (365 nm) at ambient temperature in $CDCl_3$. For an exploratory qualitative assessment of the kinetics of these reactions simple NMR spectroscopic investigations were performed and one example was explored in more detail (see below). For this purpose, small amounts of compounds **3**, **4**, **10**, **13** and **14** were dissolved in $CDCl_3$ and irradiated in an NMR tube for several hours, so that the reaction progress could be easily monitored by ^1H NMR spectroscopy. UV irradiation of the 1,5- (**3**) and 1,8-bis[(trimethylsilyl)ethynyl]-anthracene (**4**) led to a complete conversion into the corresponding [4 + 4] cycloaddition products **17** and **18**, respectively. In the case of **3** only one photodimerised species was observed and ^1H NMR spectroscopically identified as the *head to tail*-isomer, whereas a 49 : 51-mixture of the *head to head* (*syn*) and *head to tail* (*anti*) photodimers was obtained when a $CDCl_3$ solution of 1,8-bis[(trimethylsilyl)ethynyl]anthracene (**4**) was irradiated with UV light (Scheme 4). This is in accordance with the literature for the photodimerisation of 1,8-dichloroanthracene (**2**) in various solvents.[2] We did not observe the formation of a *syn–anti* mixture of photodimers when the corresponding 1,5-substituted species **3** was irradiated, although a *syn–anti* mixture was reported for 1,5-dichloroanthracene (**1**).[2]

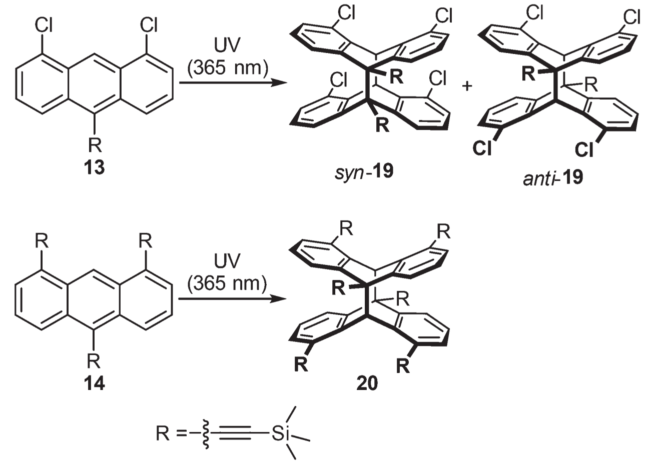
As expected, UV irradiation of the 1,8,10-substituted compound **14** led to a complete conversion into the corresponding



Scheme 3 Syntheses of the 1,8,10-trialkynylsubstituted anthracene derivatives. Reagents and conditions: (i) 1. $Me_3SiC{\equiv}CH$ (2 eq.), CuI (10 mol%), $PdCl_2(PPh_3)_2$ (5 mol%), (i-Pr)$_2$NH, reflux, 3 d; 2. aq. workup, 85%; (ii) 1. $Me_3SiC{\equiv}CMgBr$ (10 eq.), Ni(acac)$_2$, PPh_3, THF, reflux; 2. aq. workup, 83%; (iii) K_2CO_3, MeOH, r.t., 86%; (iv) Me_3SnNMe_2, THF, 60 °C, 4 h.



Scheme 4 Photodimerisation of the monomers **3** and **4** to the dimeric species **17** and **18** by UV irradiation in $CDCl_3$.



Scheme 5 Photodimerisation of the monomers **13** and **14** to the dimeric species **19** and **20** by UV irradiation in $CDCl_3$.

anti-[4 + 4] cycloaddition products **20** (Scheme 5). An increased repulsive interaction of the bulky (trimethylsilyl)ethynyl substituents might be the reason for the selective *anti*-dimerisation reaction. In contrast to that, a *syn–anti* mixture (32 : 68) of **19** was obtained when a solution of 1,8-dichloro-10-[(trimethylsilyl)ethynyl]anthracene (**13**) was irradiated under the same conditions indicating a weaker interaction of the substituents in positions 1, 8 and 10 of the *syn*-**19** isomer.

In the case of the photodimerisation of 1,8-bis[(trimethylsilyl)ethynyl]anthracene (**4**), as well as 1,8-dichloro-10-[(trimethylsilyl)ethynyl]anthracene (**13**), we determined the molecular structures in the crystalline state of the corresponding *head-to-tail* isomers *anti*-**18** (Fig. 5) and *anti*-**19** (Fig. 6), respectively.

Due to the [4 + 4] cycloaddition reaction, *anti*-**18** contains four isolated aromatic rings and an aliphatic tricyclic system. The aromatic rings are planar and the dihedral angle between their mean planes is 137.6(1)°. The phenyl C–C bond lengths and angles are ranging from 1.390(2) Å [C(6)–C(7)] to 1.407(2) Å [C(2)–C(11)] and from 119.2(2)° [C(5)–C(4)–C(9)] to 120.6(2)° [C(2)–C(11)–C(12)], respectively. As expected for sp^3 carbon atoms, the angles around C(3) and C(10) are close to tetrahedral geometry {107.9(2)° [C(9)–C(10)–C(11)] to 112.2(2)° [C(2)–C(3)–C(10′)]}. The $C(sp^3)–C_{Ph}$ distances are between 1.512(2) Å [C(10)–C(11)] and 1.519(2) Å [C(3)–C(4)], which is slightly longer than a standard $C(sp^3)–C(sp^2)$ bond (1.50 Å[12]). The C(3)–C(10′) [1.623(2) Å] bond is found to be remarkably longer than a standard $C(sp^3)–C(sp^3)$ bond (1.54 Å[1]). A repulsive interaction between the TMS-substituted alkynyl units results in an angle between the C(1)–Si(1)- and C(5)–Si(2)-vectors [15.5(1)°]. Like in the case of **4** and **8**, one of the alkynyl substituents is nearly in plane with the aryl ring it is bonded to [the C(1)-bonded in *anti*-**18**], whereas the second alkynyl unit is slightly bent, as denoted by the torsion angles C(5)–C(20)–C(21) [173.4(2)°] and C(20)–C(21)–Si(1) [173.9(2)°].

Like in the case of *anti*-**18**, the photodimer of the 10-(trimethylsilyl)ethynyl-substituted 1,8-dichloroanthracene (*anti*-

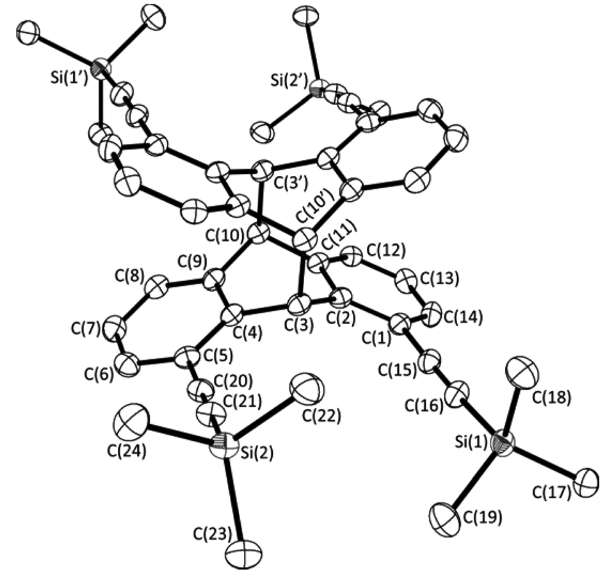


Fig. 5 Molecular structure of the *anti*-photo dimer of 1,8-bis[(trimethylsilyl)ethynyl]anthracene (*anti*-**18**). Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.398(2), C(1)–C(14) 1.406(2), C(1)–C(15) 1.445(2), C(2)–C(3) 1.517(2), C(2)–C(11) 1.407(2), C(3)–C(4) 1.519(2), C(3)–C(10′) 1.623(2), C(5)–C(20) 1.443(3), C(15)–C(16) 1.207(2), C(16)–Si(1) 1.845(2), C(20)–C(21) 1.208(2), C(21)–Si(2) 1.842(2); C(1)–C(2)–C(3) 122.4(1), C(1)–C(2)–C(11) 119.6(1), C(1)–C(15)–C(16) 179.0(1), C(2)–C(1)–C(15) 121.0(1), C(2)–C(3)–C(4) 108.3(1), C(2)–C(3)–C(10′) 112.2(1), C(4)–C(5)–C(20) 119.8(1), C(5)–C(20)–C(21) 173.4(1), C(15)–C(16)–Si(1) 175.4(1), C(20)–C(21)–Si(2) 173.9(1).

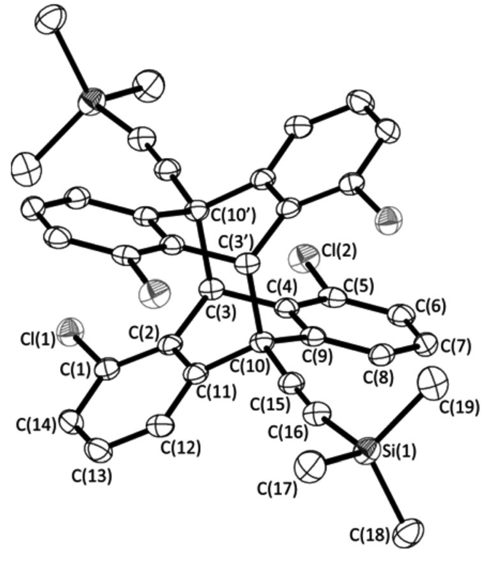


Fig. 6 Molecular structure of the *anti*-photo dimer of 1,8-bis[(trimethylsilyl)ethynyl]anthracene (*anti*-**19**). Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.391(3), C(1)–C(14) 1.391(3), C(1)–Cl(1) 1.746(2), C(2)–C(3) 1.512(2), C(2)–C(11) 1.398(3), C(3)–C(4) 1.512(3), C(3)–C(10′) 1.643(2), C(10)–C(15) 1.471(3), C(15)–C(16) 1.209(3), C(16)–Si(1) 1.840(2), C(18)–Si(1) 1.864(2); C(1)–C(2)–C(3) 123.1(2), C(1)–C(2)–C(11) 117.9(2), C(2)–C(1)–Cl(1) 120.2(1), C(2)–C(3)–C(4) 109.1(1), C(2)–C(3)–C(10′) 112.2(1), C(10)–C(15)–C(16) 176.7(2), C(11)–C(10)–C(15) 112.3(2), C(15)–C(16)–Si(1) 171.2(2).

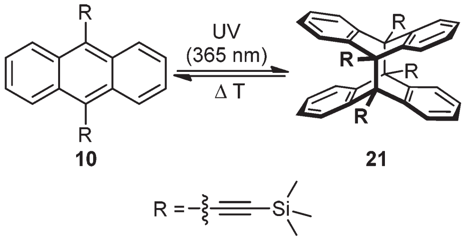
19) crystallises in the triclinic space group $P\bar{1}$ with one centrosymmetric molecule in the unit cell.

The former anthracene units are linked by their central rings, whereby the C(3)–C(10′)/C(10)–C(3′) bonds measure 1.634(2) Å, slightly longer than the corresponding ones in *anti*-**18** [1.623(2) Å] and remarkably longer than the standard C–C bond (1.54 Å[12]). The quaternary carbon atom C(10) adopts a somewhat distorted tetrahedral coordination geometry, as is indicated by its surrounding angles ranging from 106.5(2)° [C(15)–C(10)–C(3′)] to 112.3(2)° [C(15)–C(10)–C(11)]. As is indicated by the angles C(10)–C(15)–C(16) [176.7(2)°] and C(15)–C(16)–Si(1) [171.2(2)°], the alkynyl substituents deviate little from linearity. The chlorine atoms are found to be in-plane with the aromatic rings they are bonded to. The dihedral angle between these aromatic mean planes is 135.5(1)°, slightly smaller than the corresponding one in compound *anti*-**18** [137.6(1)°].

In all the cases mentioned above, a quantitative conversion into the photodimers **17**, **18**, **19** and **20** was observed and they are found to be thermally stable at ambient temperature for several weeks.

A completely different behaviour was observed, when 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**10**) was irradiated under the same conditions. Although a [4 + 4] cycloaddition reaction occurs (indicated in a new set of resonances in the ^{1}H NMR spectra), a quantitative conversion of **10** into its photodimer **21** could not be achieved (Scheme 6). Solely a maximum of 25% dimer **21** was formed after the sample was irradiated with UV light for *ca.* 4 h at ambient temperature. Anyhow, a proceeding irradiation (up to 5 hours) did not lead to an increase of the dimer-to-monomer ratio under the given circumstances.

Interestingly, we found that dimer compound **21** is much more thermally labile, compared to the other (trimethylsilyl)-ethynyl-substituted photodimers **17**, **18**, **19** and **20**, which were synthesised in this work. We investigated the kinetics of this cycloelimination reaction by a series of ^{1}H NMR experiments. Therefore, a NMR sample of 9,10-bis[(trimethylsilyl)ethynyl]-anthracene (**10**) in $CDCl_3$ was irradiated with UV light for at least 3.5 hours at ambient temperature (298 K), only interrupted for *ca.* 3 minutes by recording proton NMR spectra. After irradiation, the sample was left in the magnet at that temperature and the decay of the dimer concentration was monitored by recording its ^{1}H NMR spectra. As shown in Fig. 7, a complete cycloelimination reaction of **21** into the corresponding monomer **10** was observed after *ca.* 6.5 hours, when the sample was exposed to ambient temperature without further UV irradiation.



Scheme 6 Photodimerisation of 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**10**) to the thermally (r.t.) unstable compound **21** by UV irradiation in $CDCl_3$.

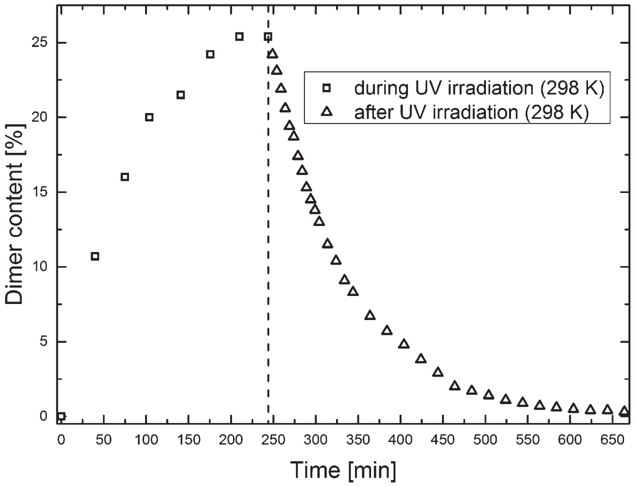


Fig. 7 Content of the photodimer **21** [%] *vs.* (irradiation-) time [min] at 298 K.

In order to monitor the influence of temperature on the monomerisation (**21** → **10**) we performed kinetic NMR experiments at 298 K, 303 K and 313 K. As can be concluded from Fig. 8, a faster decay of the dimer concentration can be observed at higher temperatures.

Starting with a photodimer-to-monomer ratio of 19.5%, a complete conversion into the monomer **10** was observed after more than 6 hours at 298 K. However, the reaction rate is remarkably increased, when the sample is held at 303 K (*ca.* 2.5 hours) or 313 K (*ca.* 1.5 hours), respectively (Fig. 8). From the data shown in Fig. 8 we could calculate an estimate for the barrier of activation E_A of 94 kJ mol^{-1}. These results suggest that 9,10-dialkynylanthracene derivatives might be

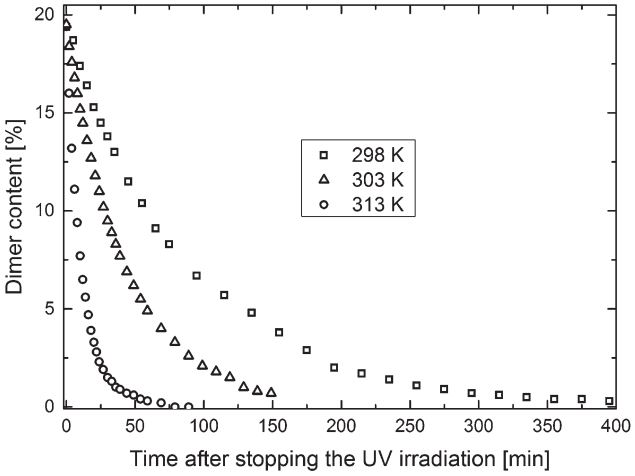


Fig. 8 Content of the photodimer **21** [%] *vs.* time after stopping the UV irradiation [min] at 298 K, 303 K and 313 K.

applicable as molecular thermo-reversible photo switching units.

Due to this interesting behaviour in solution we further assumed to dimerise 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**10**) in the solid state, according to experiments with *e.g.* diarylethene derivatives performed by Irie and coworkers.[15] For this purpose, we fixed a single crystal of **10** on a glass fibre onto the goniometer of the diffractometer. After collecting the monomer data, we used a blue-violet laser (402 nm) to irradiate the crystal (the ability of this light source for dimerisation reactions was tested by irradiating a NMR sample of **10** in $CDCl_3$). However, no photoreaction was observed by X-ray diffraction investigations, also not when the irradiation experiments were repeated several times between 243 K and 363 K. This might be due to the fact that the 9,10-disubstituted anthracenes **10** are perpendicularly oriented to each other and no π–π interactions are found in its molecular structure in the solid state.[16]

Conclusions

Anthracenes with (trimethylsilyl)ethynyl substituents in 1,5- (**3**), 1,8- (**4**) and 9,10-positions (**10**), as well as 1,8-dichloro-10-[(trimethylsilyl)ethynyl]- (**13**) and 1,8,10-tris[(trimethylsilyl)-ethynyl]anthracene (**14**) were synthesised by cross coupling reactions. In addition, 1,5- (**7**) and 1,8-bis[(trimethylstannyl) ethynyl]anthracene (**8**) have been quantitatively synthesised by conversion of the corresponding ethynyl-substituted anthracene derivatives with (dimethylamino)trimethylstannane. The $SnMe_3$-substituted dialkynes might be useful substrates in Stille type cross coupling reactions.

$CDCl_3$ solutions of the highly conjugated $SiMe_3$-substituted systems were irradiated with UV light, whereby [4 + 4] cycloaddition reactions were observed. The *anti*-isomers were selectively and quantitatively formed in the case of **3** and **14**. Irradiation of the 1,8- and 1,8,10-substituted species **4** and **13** gave *syn*–*anti* mixtures [49 : 51 (**4**); 32 : 68 (**13**)] of the photodimerised products. Interestingly, 9,10-bis[(trimethylsilyl)-ethynyl]anthracene (**10**) was found to dimerise to afford **21**, although symmetrically 9,10-substituted anthracenes with substituents, except fluorine atoms or methyl groups, are known for 28 years to be stable towards UV irradiation.[1b,6] The influence of the temperature upon monomerisation (cycloelimination) was qualitatively investigated by NMR experiments. Due to the fact that ambient temperature is sufficient for the thermally induced reaction of the photodimer **21**, 9,10-dialkynylanthracenes might be interesting objects of study *e.g.* for detailed kinetic investigations.

Experimental

General

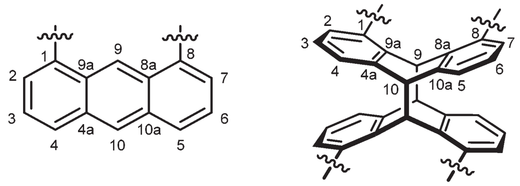
1,5- (**1**)[17] and 1,8-dichloroanthracene (**2**),[18] as well as 1,8-bis-[(trimethylsilyl)ethynyl]anthracene (**4**),[8] 1,8-diethynylanthracene (**6**),[8] 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**10**)[9] and 10-bromo-1,8-dichloroanthracene (**12**)[13] were synthesised according to literature protocols. All reactions using organometallic reagents were carried out under an anhydrous, inert atmosphere of nitrogen using standard Schlenk techniques in dry THF (dried over potassium) or *n*-hexane (dried over $LiAlH_4$). The solvents were freshly distilled before being used for the reactions. Column chromatography was performed on silica gel 60 (0.04–0.063 mm mesh). NMR spectra were recorded on a Bruker Avance III 300, a Bruker DRX 500, a Bruker Avance III 500 and a Bruker Avance 600 instrument at room temperature (298 K). The chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$: ^1H NMR $\delta = 7.26$ ppm, ^{13}C NMR $\delta = 77.16$ ppm) or referenced externally (^{29}Si: $SiMe_4$, ^{119}Sn: $SnMe_4$). EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Samples were introduced by a push rod in aluminium crucibles. Ions were accelerated by 8 kV. The numbering scheme for NMR assignments (Scheme 7) is based on IUPAC guidelines.

1,8-Dichloro-10-[(trimethylsilyl)ethynyl]anthracene (13). 10-Bromo-1,8-dichloroanthracene (200 mg, 0.61 mmol) and (trimethylsilyl)acetylene (0.7 mL, 1.22 mmol) were dissolved in diisopropylamine (40 mL). The solution was degassed by three freeze–pump–thaw cycles and CuI (12 mg, 10 mol%) and $PdCl_2(PPh_3)_2$ (22 mg, 5 mol%) were then added. After heating to reflux for 3 d, the dark brownish mixture was filtered, washed with *n*-pentane and added to water (50 mL). The aqueous layer was extracted with *n*-pentane (3 × 25 mL) and the combined organic phases were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude yellow brownish solid was purified by column chromatography (∅ = 3 cm, *l* = 20 cm, eluent: *n*-pentane). Yield: 147 mg (71%). For analytical data see ref. 14 (different synthetic protocols).

9,10-Bis[(trimethylsilyl)ethynyl]anthracene (10). Synthesis according to ref. 9; for ^1H and ^{13}C NMR data see ref. 9. $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$): $\delta = -17.17$ ppm. MS (EI, 70 eV): *m*/*z* [assignment] = 370 $[M]^+$, 355 $[M - CH_3]^+$, 297 $[M - Si(CH_3)_3]$. HRMS: calculated for $C_{24}H_{26}Si_2^+$: 370.15676; measured: 370.15800.

General procedure for Kumada coupling reactions

Trimethylsilyl acetylene ($Me_3SiC{\equiv}CH$, *ca.* 7 eq.) was added dropwise to a freshly prepared solution of ethylmagnesium bromide in THF at 0 °C. The mixture was stirred at room temp-



Scheme 7 Numbering scheme exemplarily shown for a 1,8-substituted anthracene derivative and its corresponding *anti*-photodimer.

erature for 2 h and gas evolution was observed. The [(trimethylsilyl)ethynyl]magnesium bromide suspension was transferred into a dropping funnel, fitted with glass wool for simultaneous filtering and slowly added to a solution of the dichloroanthracene derivative, Ni(acac)$_2$ and PPh$_3$ in THF at room temperature, whereby the colour of the solution changed from yellow to dark red. The mixture was heated to reflux and then quenched with a saturated aqueous solution of NH$_4$Cl. The aqueous layer was extracted with dichloromethane several times. The combined organic phases were washed with brine and dried over MgSO$_4$. The solvent was evaporated and the crude yellow brownish solid was purified by column chromatography using different eluents (see below).

1,5-Bis[(trimethylsilyl)ethynyl]anthracene (3). Synthesis according to the general procedure for Kumada coupling reactions using 1,5-dichloroanthracene (1.60 g, 6.47 mmol), PPh$_3$ and Ni(acac)$_2$ (one spatula tip of each compound), reflux for 113 h. Column chromatography (∅ = 3 cm, *l* = 25 cm, eluent: *n*-pentane–dichloromethane 8 : 1) afforded **3** as bright yellow crystals. Yield: 1.96 g (82%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.88 (s, 2H, *H*9/*H*10), 8.06 (d, $^{3}J_{\mathrm{H,H}}$ = 8.5 Hz, 2H, *H*4/*H*8), 7.74 (d, $^{3}J_{\mathrm{H,H}}$ = 6.8 Hz, 2H, *H*2/*H*6), 7.44 (dd, $^{3}J_{\mathrm{H,H}}$ = 7.0, 8.5 Hz, 2H, *H*3/*H*7), 0.39 [s, 18H, Si(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 131.65, 131.45, 131.20 (*C*2/*C*6), 130.01 (*C*4/*C*8), 125.94 (*C*9/*C*10), 125.12 (*C*3/*C*7), 120.87, 103.27 (*C*≡C–Si), 100.34 (C≡*C*–Si), 0.30 [Si(*C*H$_3$)$_3$] ppm. ^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$): δ = −17.36 ppm. MS (EI, 70 eV): *m*/*z* [assignment] = 370 [M]$^+$, 355 [M − CH$_3$]$^+$. HRMS: calculated for C$_{24}$H$_{26}$Si$_2$$^+$: 370.15676; measured: 370.15590.

1,8-Bis[(trimethylsilyl)ethynyl]anthracene (4). Synthesis according to ref. 8. Complete analytical data: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.32 (s, 1H, *H*9), 8.42 (s, 1H, *H*10), 7.98 (d, $^{3}J_{\mathrm{H,H}}$ = 8.5 Hz, 2H, *H*4/*H*5), 7.79 (d, $^{3}J_{\mathrm{H,H}}$ = 6.9 Hz, 2H, *H*2/*H*7), 7.42 (dd, $^{3}J_{\mathrm{H,H}}$ = 7.0, 9.0 Hz, 2H, *H*3/*H*6), 0.39 [s, 18H, Si(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 132.48 (*C*2/*C*6), 131.50, 131.37, 129.40 (*C*4/*C*5), 127.80 (*C*10), 125.09 (*C*3/*C*6), 124.02 (*C*9), 121.43, 103.67 (*C*≡C–Si), 99.94 (C≡*C*–Si), 0.56 [Si(*C*H$_3$)$_3$] ppm. ^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$): δ = −17.47 ppm. MS (EI, 70 eV): *m*/*z* [assignment] = 370 [M]$^+$, 355 [M − CH$_3$]$^+$, 267 [M − Si(CH$_3$)$_3$ − 2 CH$_3$]. HRMS: calculated for C$_{24}$H$_{26}$Si$_2$$^+$: 370.15676; measured: 370.15651.

1,8,10-Tris[(trimethylsilyl)ethynyl]anthracene (14). Synthesis according to the general procedure for Kumada coupling reactions using 1,8-dichloro-10-[(trimethylsilyl)ethynyl]anthracene (210 mg, 0.62 mmol), PPh$_3$ and Ni(acac)$_2$ (one spatula tip of each compound), reflux for 5 d. Column chromatography (∅ = 3 cm, *l* = 25 cm, eluent: *n*-pentane) afforded **14** as bright yellow crystals. Yield: 217 mg (83%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.35 (s, 1H, *H*9), 8.55 (d, $^{3}J_{\mathrm{H,H}}$ = 8.7 Hz, 2H, *H*4/*H*5), 7.81 (dd, $^{3}J_{\mathrm{H,H}}$ = 6.9 Hz, $^{3}J_{\mathrm{H,H}}$ = 0.7 Hz, 2H, *H*2/*H*7), 7.53 (dd, $^{3}J_{\mathrm{H,H}}$ = 7.0, 8.7 Hz, 2H, *H*3/*H*6), 0.41 [s, 9H, Si(C*H*$_3$)$_3$], 0.38 {s, 18H, [Si(C*H*$_3$)$_3$]$_2$} ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 132.82 (*C*2/*C*7), 132.70, 130.80, 128.01 (*C*4/*C*5), 126.34 (*C*3/*C*6), 125.40 (*C*9), 121.95, 118.69, 107.37 [C≡*C*–Si(CH$_3$)$_3$], 103.47 {[*C*≡C–Si(CH$_3$)$_3$]$_2$}, 101.28 [*C*≡C–Si(CH$_3$)$_3$], 100.52 {[C≡*C*–Si(CH$_3$)$_3$]$_2$}, 0.52 [Si(*C*H$_3$)$_3$], 0.34 {[Si(*C*H$_3$)$_3$]$_2$} ppm. ^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$): δ = −17.18 [*Si*(CH$_3$)$_3$], −17.35{[*Si*(CH$_3$)$_3$]$_2$} ppm. MS (EI, 70 eV): *m*/*z* [assignment] = 466 [M]$^+$, 451 [M − CH$_3$]$^+$, 394 [M − Si(CH$_3$)$_3$]$^+$. HRMS: calculated for C$_{29}$H$_{34}$Si$_3$$^+$: 466.19628; measured: 466.19757.

General procedure for the syntheses of the ethynyl-substituted compounds 5, 6, 11 and 15

The (trimethylsilyl)ethynyl substituted compounds were dissolved in an adequate amount of boiling methanol. After cooling to ambient temperature, K$_2$CO$_3$ (*ca.* 1.2 eq. per alkyne unit) was added to the mixture stirred overnight. The solvent was evaporated and the crude products were purified by column chromatography.

1,5-Diethynylanthracene (5). Synthesis according to the general procedure using 1,5-bis[(trimethylsilyl)ethynyl]anthracene (1.70 g, 4.59 mmol) and K$_2$CO$_3$ (1.14 g, 8.25 mmol) in MeOH (450 mL). Column chromatography (∅ = 3 cm, *l* = 11 cm, eluent: *n*-pentane) afforded **5** as bright yellow crystals. Yield: 0.96 g (93%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.93 (s, 2H, *H*9/*H*10), 8.10 (d, $^{3}J_{\mathrm{H,H}}$ = 8.6 Hz, 2H, *H*4/*H*8), 7.79 (d, $^{3}J_{\mathrm{H,H}}$ = 6.8 Hz, 2H, *H*2/*H*6), 7.46 (dd, $^{3}J_{\mathrm{H,H}}$ = 7.0, 8.4 Hz, 2H, *H*3/*H*7), 3.60 (s, 2H, C≡C–*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 131.74 (*C*2/*C*6), 131.70, 131.51, 130.20 (*C*4/*C*8), 125.78 (*C*9/*C*10), 125.15 (*C*3/*C*7), 119.92, 82.72 (C≡*C*–H), 81.94 (*C*≡C–H) ppm. MS (EI, 70 eV): *m*/*z* [assignment] = 226 [M]$^+$, 200 [M − CCH]$^+$. HRMS: calculated for C$_{18}$H$_{10}$$^+$: 226.07770; measured: 226.07662.

1,8-Diethynylanthracene (6). Synthesis according to ref. 8. Complete analytical data: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.44 (s, 1H, *H*9), 8.45 (s, 1H, *H*10), 8.03 (d, $^{3}J_{\mathrm{H,H}}$ = 8.6 Hz, 2H, *H*4/*H*5), 7.80 (d, $^{3}J_{\mathrm{H,H}}$ = 6.8 Hz, 2H, *H*2/*H*7), 7.45 (dd, $^{3}J_{\mathrm{H,H}}$ = 7.0, 8.5 Hz, 2H, *H*3/*H*6), 3.62 (s, 2H, C≡C–*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 131.72 (*C*2/*C*6), 131.47, 129.61 (*C*4/*C*5), 127.67 (*C*10), 125.14 (*C*3/*C*6), 123.90 (*C*9), 120.49, 82.78 (C≡*C*–H), 81.81 (*C*≡C–H) ppm. MS (EI, 70 eV): *m*/*z* [assignment] = 226 [M]$^+$. HRMS: calculated for C$_{18}$H$_{10}$$^+$: 226.07770; measured: 226.07599.

9,10-Diethynylanthracene (11). Synthesis according to the general procedure using 9,10-bis[(trimethylsilyl)ethynyl]anthracene (0.45 g, 1.2 mmol) and K$_2$CO$_3$ (0.42 g, 3.0 mmol) in MeOH (250 mL). Column chromatography (∅ = 3 cm, *l* = 9 cm, eluent: *n*-pentane) afforded **11** as a yellow-brownish solid. Yield: 71 mg (25%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.62 (m, 6H, *H*1/*H*4/*H*5/*H*8), 7.63 (m, 6H, *H*2/*H*3/*H*6/*H*7), 4.07 (s, 2H, C≡C–*H*) ppm. ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$): δ = 132.62, 127.19, 127.17, 117.96, 90.01 (C≡*C*–H), 80.35 (*C*≡C–H) ppm. MS (EI, 70 eV): *m*/*z* [assignment] = 226 [M]$^+$, 198 [M − CCH]$^+$. HRMS: calculated for C$_{18}$H$_{10}$$^+$: 226.07770; measured: 226.07663.

1,8,10-Triethynylanthracene (15). Synthesis according to the general procedure using 1,8,10-tris[(trimethylsilyl)ethynyl]anthracene (0.48 g, 1.03 mmol) and K$_2$CO$_3$ (0.24 g, 1.75 mmol) in MeOH (80 mL). Column chromatography (∅ = 3 cm, *l* = 8 cm, eluent: *n*-pentane) afforded **15** as a bright yellow solid. Yield: 0.22 g (86%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.52 (s, 1H, *H*9), 8.61 (d, $^{3}J_{\mathrm{H,H}}$ = 8.8 Hz, 2H, *H*4/*H*5), 7.83 (d, $^{3}J_{\mathrm{H,H}}$ = 6.8 Hz, 2H, *H*2/*H*7), 7.56 (dd, $^{3}J_{\mathrm{H,H}}$ = 7.0, 8.7 Hz, 2H, *H*3/*H*6), 4.02 (s, 1H, C≡C–*H*), 3.63 [s, 2H, (C≡C–*H*)$_2$] ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 132.79, 131.80 (*C*2/*C*7), 127.94 (*C*4/*C*5), 126.18 (*C*3/*C*6), 125.80 (*C*9), 120.74, 89.04 (C≡*C*–H), 83.10 [(C≡*C*–H)$_2$], 81.32 [(*C*≡C–H)$_2$], 79.86 (*C*≡C–H) ppm. MS (EI, 70 eV): *m*/*z* [assignment] = 250 [M]$^+$, 224 [M − CCH]$^+$. HRMS: calculated for $C_{20}H_{10}^{+}$: 250.07770; measured: 250.07795.

General procedure for the syntheses of the trimethylstannyl-substituted compounds 7, 8 and 16

The $SnMe_3$ functionalisation of the ethynyl substituted compounds was carried out analogous to a procedure described by Wrackmeyer and coworkers.[19] The corresponding ethynylanthracene derivatives were dissolved in a small amount of dry THF. (Dimethylamino)trimethylstannane (*ca.* 2 eq. per alkyne unit) was added dropwise to the solution and the mixture was heated to 60 °C for 4 h. After cooling to ambient temperature, all volatile compounds were removed *in vacuo* and the desired species were quantitatively obtained as yellow solids. Single crystals of **7** and **8**, suitable for X-ray diffraction experiments were afforded after recrystallisation from dry *n*-hexane.

1,5-Bis[(trimethylstannyl)ethynyl]anthracene (7). Synthesis according to the general procedure using 1,5-diethynylanthracene (20 mg, 0.09 mmol), (dimethylamino)trimethylstannane (0.08 mL, 0.49 mmol) and THF (6 mL). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.93 (s, 2H, *H*9/*H*10), 8.04 (d, $^{3}J_{\mathrm{H,H}}$ = 8.7 Hz, 2H, *H*4/*H*8), 7.72 (m, 2H, *H*2/*H*6), 7.42 (dd, $^{3}J_{\mathrm{H,H}}$ = 6.9, 8.5 Hz, 2H, *H*3/*H*7), 0.48 [s, 18H, Sn(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 131.69, 131.53, 130.84 (*C*2/*C*6), 129.54 (*C*4/*C*8), 126.04 (*C*9/*C*10), 125.11 (*C*3/*C*7), 121.36, 107.04 (*C*≡C–Sn), 99.77 (C≡*C*–Sn), −7.30 [Sn(*C*H$_3$)$_3$] ppm. ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$): δ = −63.15 ppm. MS (EI, 70 eV): *m*/*z* [assignment] = 552 [M]$^+$, 537 [M − CH$_3$]$^+$, 226 [M − 2(SnCH$_3$)$_3$]$^+$. HRMS: calculated for $C_{24}H_{26}Sn_2^{+}$: 554.00730; measured: 554.00711.

1,8-Bis[(trimethylstannyl)ethynyl]anthracene (8). Synthesis according to the general procedure using 1,8-diethynylanthracene (26 mg, 0.11 mmol), (dimethylamino)trimethylstannane (0.11 mL, 0.70 mmol) and THF (6 mL). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.43 (s, 1H, *H*9), 8.40 (s, 1H, *H*10), 7.95 (d, $^{3}J_{\mathrm{H,H}}$ = 8.4 Hz, 2H, *H*4/*H*5), 7.76 (dd, $^{3}J_{\mathrm{H,H}}$ = 6.9 Hz, $^{4}J_{\mathrm{H,H}}$ = 1.0 Hz, 2H, *H*2/*H*7), 7.40 (dd, $^{3}J_{\mathrm{H,H}}$ = 6.9, 8.5 Hz, 2H, *H*3/*H*6), 0.46 [s, 18H, Sn(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 131.77 (*C*2/*C*7), 131.57, 131.51, 128.92 (*C*4/*C*5), 127.58 (*C*10), 125.10 (*C*3/*C*6), 124.44 (*C*9), 107.43 (*C*≡C–Sn), 99.27 (C≡*C*–Sn), −6.99 [Sn(*C*H$_3$)$_3$] ppm. ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$): δ = −63.98 ppm. MS (EI, 70 eV): *m*/*z* [assignment] = 552 [M]$^+$, 537 [M − CH$_3$]$^+$, 390 [M − Sn(CH$_3$)$_3$]$^+$, 345 [M − Sn(CH$_3$)$_3$ − 3CH$_3$]$^+$, 224 [M − 2(SnCH$_3$)$_3$]$^+$. HRMS: calculated for $C_{24}H_{26}Sn_2^{+}$: 554.00730; measured: 554.00760.

1,8,10-Tris[(trimethylstannyl)ethynyl]anthracene (16). Synthesis according to the general procedure using 1,8,10-triethynylanthracene (20 mg, 0.08 mmol), (dimethylamino)trimethyltin (0.1 mL, 0.6 mmol) and THF (19 mL). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.44 (s, 1H, *H*9), 8.58 (d, $^{3}J_{\mathrm{H,H}}$ = 8.7 Hz, 2H, *H*4/*H*5), 7.78 (d, $^{3}J_{\mathrm{H,H}}$ = 6.5 Hz, 2H, *H*2/*H*7), 7.49 (dd, $^{3}J_{\mathrm{H,H}}$ = 7.0, 8.7 Hz, 2H, *H*3/*H*6), 0.49 [s, 9H, Sn(C*H*$_3$)$_3$], 0.46 {s, 18H, [Sn(C*H*$_3$)$_3$]$_2$} ppm. Due to rapid decomposition to the reactant **15** under the experimental conditions, no further characterisation of the product could be performed.

General procedure for photodimerisation reactions

Small amounts of the (trimethylsilyl)ethynyl substituted compounds **3**, **4**, **10**, **13** and **14** were dissolved in $CDCl_3$ (*ca.* 0.55 mL) and irradiated with UV light (365 nm, UVP, UVGL-25 Compact UV Lamp 254/365 nm, 4 W) in an NMR tube for several hours.

Photodimerisation of 1,5-bis[(trimethylsilyl)ethynyl]anthracene. Synthesis according to the general procedure. Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (m, 8H, *H*4/*H*8/*H*2/*H*6), 7.44 (dd, $^{3}J_{\mathrm{H,H}}$ = 7.2, 8.1 Hz, 4H, *H*3/*H*7), 6.38 (s, 4H, *H*9/*H*10), 0.31 [s, 36H, Si(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 139.93, 137.81, 131.17, 127.80 (*C*3/*C*7), 124.03, 118.87, 100.74 (*C*≡C–Si), 99.81 (C≡*C*–Si), 77.00 (*C*9/*C*10), 0.12 [Si(*C*H$_3$)$_3$] ppm. ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = −17.03 ppm.

Photodimerisation of 1,8-bis[(trimethylsilyl)ethynyl]anthracene. Synthesis according to the general procedure gives a *syn*–*anti* mixture (49 : 51) of the photodimerised species. Analytical data for the *syn*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.43 (d, $^{3}J_{\mathrm{H,H}}$ = 7.9 Hz, 4H, *H*2/*H*7), 7.35 (d, $^{3}J_{\mathrm{H,H}}$ = 7.2 Hz, 4H, *H*4/*H*5), 7.22 (m, 4H, *H*3/*H*6), 6.79 (s, 2H, *H*9), 5.96 (s, 2H, *H*10), 0.38 [s, 36H, Si(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 138.30, 132.78 (*C*2/*C*7), 127.78 (*C*3/*C*6), 123.66 (*C*4/*C*5), 119.49, 101.28 (*C*≡C–Si), 98.14 (C≡*C*–Si), 78.95 (*C*10), 75.27 (*C*9), 0.63 [Si(*C*H$_3$)$_3$] ppm. One signal missing due to overlap or line broadening. ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = −17.08 ppm. Analytical data for the *anti*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.03 (d, $^{3}J_{\mathrm{H,H}}$ = 7.3 Hz, 4H, *H*4/*H*5), 6.97 (dd, $^{3}J_{\mathrm{H,H}}$ = 8.0 Hz, $^{4}J_{\mathrm{H,H}}$ = 0.8 Hz, 4H, *H*2/*H*7), 6.80 (m, 4H, *H*3/*H*6), 5.54 (d, $^{3}J_{\mathrm{H,H}}$ = 11.0 Hz, 2H, *H*9), 4.54 (d, $^{3}J_{\mathrm{H,H}}$ = 10.9 Hz, 2H, *H*10), 0.31 [s, 36H, Si(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 144.14, 143.37, 130.25 (*C*2/*C*7), 126.40 (*C*4/*C*5), 125.74 (*C*3/*C*6), 121.83, 104.52 (*C*≡C–Si), 99.67 (C≡*C*–Si), 52.23 (*C*9), 48.74 (*C*10), 0.35 [Si(*C*H$_3$)$_3$] ppm. One signal missing due to overlap or line broadening. ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = −17.83 ppm.

Photodimerisation of 9,10-bis[(trimethylsilyl)ethynyl]anthracene. Synthesis according to the general procedure. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.69 (m, 8H, *H*1/*H*4/*H*5/*H*8), 7.37 (m, 8H, *H*2/*H*3/*H*6/*H*7), 0.38 [s, 36H, Si(C*H*$_3$)$_3$] ppm. Due to the fast cycloelimination reaction, ^{13}C NMR shifts of the photodimerised compound **21** were determined by ^{1}H,^{13}C HMBC and HSQC experiments at 278 K in $CDCl_3$. δ = 136.86, 128.06, 122.82, 101.53, 79.08 (*C*9/*C*10) ppm. Signals missing due to overlap or line broadening.

Photodimerisation of 1,8-dichloro-10-[(trimethylsilyl)-ethynyl]anthracene. Synthesis according to the general procedure gives a *syn*–*anti* mixture (32 : 68) of the photodimerised species. Analytical data for the *syn*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.59 (d, $^{3}J_{\mathrm{H,H}}$ = 7.3 Hz, 4H, *H*4/*H*5), 7.35 (d,

Table 5 Crystallographic data for **3**, **4**, **5**, **7**, **8**, *anti*-**18** and *anti*-**19**

	3	**4**	**5**	**7**	**8**	*anti*-**18**	*anti*-**19**
Emp. formula	$C_{24}H_{26}Si_2$	$C_{24}H_{26}Si_2$	$C_{18}H_{10}$	$C_{24}H_{26}Sn_2$	$C_{102}H_{118}Sn_8$	$C_{48}H_{52}Si_4$	$C_{38}H_{32}Cl_4Si_2$
M_r	370.63	370.63	226.26	551.83	2293.48	741.26	686.62
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	1.54178	0.71073
T [K]	100.0	100(2)	100.0(2)	100.0(1)	100.0(1)	100(2)	100(2)
$F(000)$	396	1584	472	540	2260	396	356
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.26970(2)	23.6928(2)	10.93715(2)	11.4064(2)	15.3809(3)	8.564(3)	7.5761(6)
b [Å]	5.81937(7)	8.6313(1)	11.26203(2)	6.07068(1)	15.4149(3)	10.244(4)	10.0339(8)
c [Å]	16.56046(2)	24.1592(2)	9.96535(2)	16.7481(4)	21.7315(4)	12.957(5)	12.7454(8)
α [°]	90	90	90	90	80.698(2)	79.45(3)	110.973(5)
β [°]	99.6391(1)	117.0424(5)	105.9353(2)	94.669(2)	74.637(2)	82.01(2)	99.303(5)
γ [°]	90	90	90	90	86.960(2)	76.34(1)	101.673(4)
V [Å^3]	1070.74(2)	4400.40(7)	1180.31(3)	1122.46(4)	4902.7(2)	1080.5(7)	856.5(1)
Z	2	8	4	2	2	1	1
$\rho_{calcd.}$ [g cm^{-3}]	1.150	1.119	1.273	1.633	1.554	1.139	1.331
μ [mm^{-1}]	0.170	0.166	0.072	2.229	2.045	1.502	0.442
θ_{max} [°]	30.30	27.49	30.03	30.00	30.00	72.42	25.00
Index ranges h	$-15 \le h \le 15$	$-30 \le h \le 30$	$-15 \le h \le 15$	$-16 \le h \le 16$	$-21 \le h \le 21$	$-10 \le h \le 10$	$-9 \le h \le 9$
Index ranges k	$-8 \le k \le 8$	$-11 \le k \le 11$	$-15 \le k \le 15$	$-8 \le k \le 8$	$-21 \le k \le 21$	$-12 \le k \le 12$	$-11 \le k \le 11$
Index ranges l	$-23 \le l \le 23$	$-31 \le l \le 31$	$-14 \le l \le 14$	$-23 \le l \le 23$	$-30 \le l \le 30$	$-15 \le l \le 15$	$-15 \le l \le 14$
Refl. collected	59 469	93 358	67 142	47 899	85 614	20 419	11 464
Indep. refl.	3116	10 078	3436	3274	28 567	4051	2930
R_{int}	0.0343	0.034	0.0433	0.0393	0.0256	0.0300	0.044
Observed refl., $I > 2\sigma(I)$	2870	8795	2987	2966	24 838	3821	2605
Parameters	121	481	163	121	1017	241	202
R_1, $I > 2\sigma(I)$	0.0327	0.0335	0.0428	0.0225	0.0238	0.0335	0.0347
wR_2, $I > 2\sigma(I)$	0.0937	0.0936	0.1229	0.0532	0.0465	0.0901	0.0876
R_1 (all data)	0.0352	0.0395	0.0489	0.0260	0.0311	0.0350	0.0398
wR_2 (all data)	0.0963	0.0980	0.1277	0.0558	0.0490	0.0912	0.0915
GoF	1.063	1.039	1.068	1.068	1.032	1.062	1.039
ρ_{max}/ρ_{min} [e Å^{-3}]	0.43/−0.19	0.33/−0.30	0.43/−0.18	1.07/−0.60	0.53/−0.54	0.41/−0.20	0.28/−0.33
Remarks	—	—	—	—	[a]	—	—
CCDC number	994028	994029	994030	994031	994032	994033	994034

[a] Four molecules of **8** and one molecule of *n*-hexane are found in the asymmetric unit.

$^3J_{H,H}$ = 7.5 Hz, 4H, *H*2/*H*7), 7.29 (m, 4H, *H*3/*H*6), 6.89 (s, 2H, H9), 0.37 [s, 18H, Si(CH_3)$_3$]. $^{13}C\{^1H\}$ NMR (125 MHz, CDCl$_3$): δ = 139.97, 134.66, 129.48, 129.22 (*C*3/*C*6), 129.05 (*C*2/*C*7), 121.56 (*C*4/*C*5), 102.52 (*C*≡C–Si), 92.58 (C≡*C*–Si), 73.61 (*C*9), −0.13 [Si(*C*H$_3$)$_3$] ppm. *C*10 signal was missing due to overlap or line broadening. $^{29}Si\{^1H\}$ NMR (99 MHz, CDCl$_3$): δ = −15.21 ppm. Analytical data for the *anti*-isomer: ^1H NMR (500 MHz, CDCl$_3$, 298 K): δ = 7.70 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.0 Hz, 4H, *H*4/*H*5), 6.95 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.2 Hz, 4H, *H*2/*H*7), 6.91 (m, 4H, *H*3/*H*6), 5.99 (s, 2H, *H*9), 0.38 [s, 18H, Si(CH_3)$_3$]. $^{13}C\{^1H\}$ NMR (125 MHz, CDCl$_3$): δ = 143.74, 136.89, 133.33, 127.68 (*C*3/*C*6), 127.52 (*C*2/*C*7), 124.04 (*C*4/*C*5), 106.61 (*C*≡C–Si), 94.96 (C≡*C*–Si), 56.08 (*C*9), 53.75 (*C*10), 0.26 [Si(*C*H$_3$)$_3$] ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, CDCl$_3$): δ = −17.18 ppm.

Photodimerisation of 1,8,10-tris[(trimethylsilyl)ethynyl]-anthracene. Synthesis according to the general procedure. Analytical data: ^1H NMR (500 MHz, CDCl$_3$, 298 K): δ = 7.63 (d, $^3J_{H,H}$ = 7.2 Hz, 4H, *H*2/*H*7), 7.45 (dd, $^3J_{H,H}$ = 1.1, 7.9 Hz, 4H, *H*4/*H*5), 7.27 (m, 4H, *H*3/*H*6), 6.81 (s, 2H, *H*10), 0.36 {s, 18H, [Si(CH_3)$_3$]$_2$}, 0.30 {s, 36H, [Si(CH_3)$_3$]$_4$} ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CDCl$_3$): δ = 138.37, 137.50, 133.16 (*C*4/*C*5), 127.72 (*C*3/*C*6), 122.83 (*C*2/*C*7), 119.22, 101.24 {[C≡*C*–Si(CH$_3$)$_3$]$_2$}, 99.74 {[C≡*C*–Si(CH$_3$)$_3$]$_4$}, 75.72 (*C*10), 0.35 {[Si(*C*H$_3$)$_3$]$_4$}, 0.09 {[Si(*C*H$_3$)$_3$]$_2$} ppm. Signals were missing due to overlap or line broadening. $^{29}Si\{^1H\}$ NMR (99 MHz, CDCl$_3$): δ = −15.45 [*Si*(CH$_3$)$_3$], −17.08 {[*Si*(CH$_3$)$_3$]$_2$} ppm.

Crystal structure determination

Suitable crystals of the compounds **3**, **4**, **5**, **7**, **8**, *anti*-**18**, and *anti*-**19** were obtained by recrystallisation of dry *n*-hexane (**7** and **8**), by slow evaporation of saturated solutions of *n*-pentane (**5** and *anti*-**19**), *n*-pentane/dichloromethane (**3** and **4**) and chloroform (*anti*-**18**). They were selected, coated with paratone-N oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen gas cold stream solidifying the oil. Data collection was performed on a SuperNova, Dual, Cu at zero, Atlas diffractometer (**3**, **7** and **8**), a SuperNova, Single Source at Offset, Eos diffractometer (**5**), a Nonius KappaCCD diffractometer (**4** and *anti*-**19**) and a Bruker AXS X8 ProspectorUltra with APEX II diffractometer (*anti*-**18**).

The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97).[20] Crystal and refinement details, as well as CCDC numbers are provided in Table 5. CCDC 994028–994034 contain the supplementary crystallographic data for this paper.

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