

The design of UV absorbing systems for horticultural applications

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Research Article

The Design of UV Absorbing Systems for Horticultural Applications

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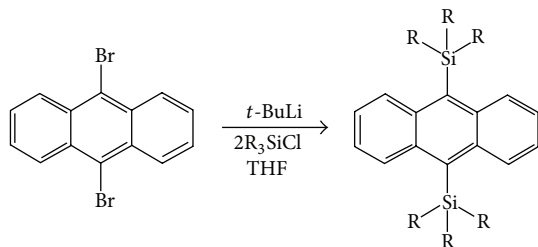
The synthesis and fluorescence behavior of a series of bis(trisilylalkyl)anthracene molecules is described. The photodegradation of these molecules under UV light has been monitored and compared to a commercially available fluorescent optical brightener. There is a relationship between the structure and the rate of photo decay. The materials with more bulky substituents exhibit the greater stability towards UV. For bis(triphenylsilyl)anthracene the photostability appears to be comparable with a commercially available optical brightener, but the molecule may be susceptible to thermal decay.

1. Introduction

The development of environmentally friendly routes towards improved crop production is a goal of global concern. One particularly attractive proposition studied by a number of groups including the team at Reading, is the development of spectral filters in polyethylene cladding used for commercially grown protected crops. For example, a reduction in plant height has been observed in a range of species under polyethylene films containing a far-red blocking dye, thereby, offering an alternative method of producing compact high quality plants without using chemical growth regulators [1–4]. In this approach the polymer film controls the red/far red light balance by means of a phthalocyanine dye system absorbing in a narrow band at 730 nm. The dye is designed to be soluble in polyethylene, and thus plants can be grown in a horticultural tunnel with low levels of far red light.

In this paper we extend our studies into modifying the film's absorption in the short wavelength end of the visible spectrum. It has been shown that UV blocking films may provide an environmentally friendly way of reducing pests and disease; for example, it has been found that whitefly incidence is considerably reduced for crops grown under such films [5]. In addition, it has been shown that the presence of

UVB and UVA radiation increases the presence of phenolic compounds in Lollo Rosso lettuce albeit with a considerable reduction in plant mass [6]. In this presentation we discuss the further application of the production of films which absorb near ultraviolet radiation and which fluoresce in the short-wavelength visible region. Such films have been found to reduce the sporulation of *Botrytis cinerea* in crops grown in horticultural tunnels [7]. Initial studies of these films with commercially available fluorescent materials as additives for polyethylene cladding for horticultural tunnels have revealed a number of difficulties, the most obvious of which is the limited lifetime of the chromophore, particularly in the presence of bright sunlight. Thus such films were found to have useful lifetimes of only approximately 6 months which may be sufficient for one season but not commercially attractive as longer-lasting films. In the case of the far-red absorbing films designed above, it was possible to extend the lifetime of the chromophore by the introduction of a Cu(II) ion to the phthalocyanine dye; presumably the central metal ion reduced the triplet lifetime of the excited state [8] and thereby reduced the chance of singlet oxygen formation [9]; in view of the need for fluorescence for the present application, this method would not be applicable. In this paper we explore one particular class of chromophores, namely,



SCHEME 1: Synthetic route to 9,10-disilylanthracene.

the 9,10-disilylanthracene system as a model to investigate the factors which control the lifetimes of such materials when used as spectral filters.

2. Results and Discussion

2.1. Synthesis. A number of reports of the preparation of bis(alkylsilyl)anthracenes appear in the literature, particularly the bis(trimethylsilyl)anthracene [10–14]. In these investigations, a series of 9,10 bis(trialkylsilyl)anthracenes were synthesized with modifications to the method described by Kyushin et al. (Scheme 1) [15] which uses the reaction of 9,10-dibromoanthracene with *tert*-butyllithium followed by addition of the dicarbanion intermediate to the appropriate trialkyl/arylsilyl chloride. The products were recrystallized twice with a minimum amount of ethanol in order to remove traces of anthracene and other starting materials which were evident in the ^1H NMR spectrum of the crude material. The yields for the bis(trimethylsilyl)- and bis(triethylsilyl)anthracenes were satisfactory, while those for the propyl and butyl analogues were poor; although no attempt was made to maximize yields in these cases, we note that the introduction of bulky groups in these systems seemed problematic. This was particularly apparent in the case of 9,10-bis(triphenylsilyl)anthracene. Karatsu et al. [16] report the synthesis of this material and its potential as an electroluminescent material in our hands; some difficulties were encountered in the preparation of this material, and a number of modifications were examined. Initial attempts yielded material heavily contaminated with anthracene, suggesting that the reaction of the first formed anion with triphenylsilyl chloride was slow, not unreasonable in view of the steric crowding present. On other occasions the di-substituted material was obtained, but this was heavily contaminated with the mono-substituted derivative. The successful synthesis of this material relied on the careful purification and drying of the triphenylsilyl chloride; even here the material was heavily contaminated with the mono-substituted material, and the two could be only isolated by chromatography. A further complication was apparent in that the NMR of the material in solution changed with time; in particular it was found that on standing signals from anthracene became apparent suggesting substantial thermal instability.

TABLE 1: Absorption characteristics for 9,10-bis(trialkyl/triphenylsilyl)anthracenes.

Functional alkyl/aryl group	Absorption (λ_{max} /nm)
Methyl ^a	402
Ethyl ^a	406
Propyl ^a	407
Butyl ^a	408
Phenyl ^b	415

^aIn hexane, ^bdissolved in DCM.

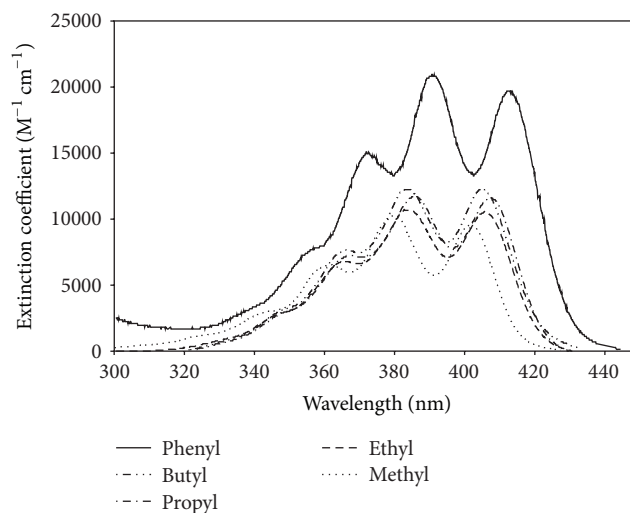


FIGURE 1: UV spectra of the bis(trialkyl/triphenylsilyl)anthracenes synthesized in this work.

2.2. Absorption Properties of 9,10-Bis(trialkyl/triphenylsilyl)anthracenes. The absorption spectra of the 9,10-bis(trialkyl/triphenylsilyl)anthracenes showed a distinctive three-peak system as shown in Figure 1. This peak pattern is characteristic of anthracene compounds, and the influence of alkyl/aryl substitution on the spectrum is shown in Table 1. This effect may be attributed to the interaction of the σ orbitals of the silicon in the 9-10 positions with the π orbitals of the aromatic ring in the excited state. As Table 1 shows there is a small but systematic increase in λ_{max} with increasing size of the substituent, but it should be noted that the phenyl derivative was poorly soluble in hexane, and in this case dichloromethane was used as the solvent.

The fluorescence spectra of the bis(triphenyl)anthracene is shown in Figure 2. In general these compounds were strongly fluorescent, in agreement with studies that have suggested that silyl substituted anthracenes have high quantum yields of fluorescence [17] which is attributed to inhibition of the decay of the S_1 state by intersystem crossing to the T_1 [18]. The fluorescence of these compounds occurred in the 400 to 550 nm region with an emission maximum at 438 nm.

2.3. Photodegradation of (Trialkyl/triphenylsilyl)anthracenes in Solution. 9,10-Bis(trialkylsilyl/triphenylsilyl)anthracenes were investigated for their relative photostabilities by using the unfiltered radiation from a medium pressure mercury

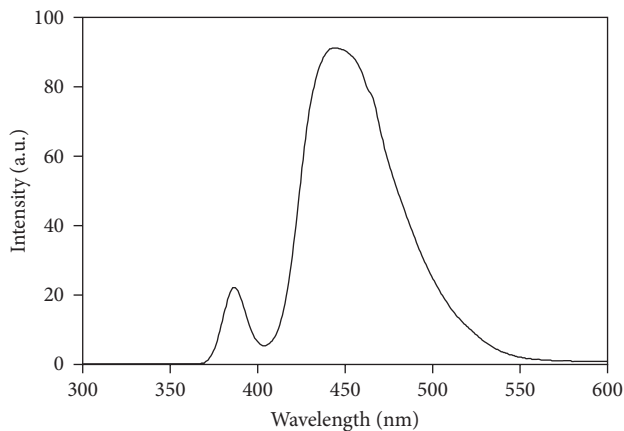


FIGURE 2: UV/visible and fluorescence spectra for 9,10-bis(triphenylsilyl)anthracene.

arc lamp (see Section 4). The decrease in absorbance at *ca.* 400 nm of the anthracenes as a function of time was analyzed. It was observed that the decay was first order with reference to the chromophore concentration. The results for solutions of the chromophore in hexane (hexane was chosen as it was considered to be close to polyethylene in terms of its solvation properties) are shown in Table 2. As inspection shows, the rate of decay decreases with the introduction of bulkier substituents; the most significant difference is that the triethylsilyl compound is much less photolabile than the analogous trimethylsilyl compound. The difference between the three longer chain alkyl groups is, by comparison, too small to be considered significant within the limitations of these experiments. The triphenyl derivative exhibited a marked increase in stability, but it should be noted that some decay in the absence of light was observed. As a comparison, we examined the decay of a commercially available “optical brightener” (UVITEX OB (Ciba)); we have previously shown that in the field, as a solution in polyethylene, this material had a useful lifetime of *ca.* 6 months. Irradiation of the solution in hexane in a similar way to that used for the other samples showed a substantially greater stability; on the basis of irradiation for 6 hours, we were able to extrapolate a half-life of some 415,000 seconds. This value is over 50 times more stable; thus, on this basis we might expect a lifetime in the field as a film for the most stable of the chromophores of 3-4 days. On this basis, these anthracene derivatives may appear, at first, unpromising; however, the lifetimes could be improved significantly by the addition of stabilizing agents as discussed below.

In order to gain a better understanding of the degradation processes, an attempt was made to analyze the photoproducts, specifically for the ethyl-silylo-substituted compound. Analysis of the photoproduct by mass spectrometry gave a parent ion of 438 amu (9,10-bis(triethylsilyl)anthracene has a molar mass of 406 amu). The additional mass is highly suggestive of endoperoxide formation at 9,10 positions [19] of the disilylanthracene, a process which is well-known and well-characterized in anthracenes. Although it was not possible

TABLE 2: Summary of kinetic data for 9,10-bis(trialkyl/triphenylsilyl)anthracenes.

Functional alkyl/aryl group	Rate constant (k) s^{-1}	Half-life ($T_{1/2}$) seconds
Methyl ^a	9.3×10^{-4}	744
Ethyl ^a	3.4×10^{-4}	2059
Propyl ^a	2.95×10^{-4}	2346
Butyl ^a	2.8×10^{-4}	2461
Phenyl ^b	9×10^{-5}	7702

^aIn hexane, ^bdissolved in DCM.

TABLE 3: Kinetic measurements of 9,10-bis(triethylsilyl)anthracene in solution in the presence and absence of oxygen.

	Rate constant (k) s^{-1}	Half-life ($T_{1/2}$) seconds
Absence of oxygen (in solution)	3.7×10^{-4}	1856.4
Presence of oxygen (in solution)	4.4×10^{-4}	1596

to record an accurate mass for the product and no ¹H NMR spectrum could be obtained due to the low stability of the product, its formation does suggest that oxygen is involved in the photo process, and consequently the effect of oxygen was monitored.

2.4. Effect of Oxygen. The effect of oxygen on the photoprocess was further explored by the irradiation of 9,10-bis(triethylsilyl)anthracene under aerated and deaerated conditions. Oxygen was removed from the solution (hexane 1 mg/10 mL) by a freeze-pump-thaw/purging process (see Section 4), and irradiation of this was compared with an identical system in which no attempt was made to remove oxygen. The results are given in Table 3 from which it can be seen that even within the limited precision of these measurements the presence of oxygen accelerates the photo degradation, but the differences in the rate constants and the half-lives are not large which suggest that this is unlikely to be the major mechanism for photo decay.

2.5. Effect of Physical Quenching Agents. The photo degradation behavior of the anthracene chromophores was investigated with two photostabilizers, firstly 4-methyl-2,6-di-*tert*-butylphenol (BHT), which is a phenolic free radical scavenger and 1,4-diazabicyclo[2.2.2]octane (DABCO), which is known to quench singlet oxygen and has negligible influence on free radical reactions [20]. The BHT data were obtained simultaneously with the data for the unstabilized materials. The results were largely insignificant for the phenolic inhibitor (Table 4); with the exception of the bis(triphenylsilyl) derivative, here, a log plot shows a significant reduction in the rate of decomposition with BHT with the half-life increasing by an order of magnitude. DABCO had a small but consistent effect on the rate of photo decay of all the bis(trialkylsilyl)anthracenes, and this increased with increasing concentration of the singlet oxygen

TABLE 4: Summary of kinetic data for 9,10-bis(trialkyl/triphenylsilyl)anthracenes with BHT.

Type of alkyl/aryl group	Rate constant (+BHT) (k) s^{-1}	Half-life ($T_{1/2}$) seconds (+BHT)
Methyl	8.7×10^{-4}	798
Ethyl	3.2×10^{-4}	2189
Propyl	2.9×10^{-4}	2388
Butyl	2.6×10^{-4}	2632
Phenyl ^a	6.7×10^{-6}	103972

^aDissolved in dichloromethane.

TABLE 5: Kinetic measurements of 9,10-bis(triethylsilyl)anthracene in films in the presence/absence of oxygen.

	Rate constant (k) s^{-1}	Half-life ($T_{1/2}$) seconds
Absence of oxygen (PMMA film)	8.3×10^{-6}	83160
Presence of oxygen (PMMA film)	1.2×10^{-5}	59400

quencher, adding further weight to the idea that oxygen (via singlet oxygen) provides a partial, but not the main, route to photodecomposition. A far more likely avenue for the loss of the anthracene is its photodimerization [21].

The significant increase in the photostability of the phenyl silyl anthracene is consistent with the report that bulky substituents, such as the triphenylsilyl groups, on the 9,10-positions of anthracenes produce a significant increase in fluorescence quantum yield [16]. Photodimerization of meso-substituted anthracenes leading to head-to-tail (HT) and head-to-head (HH) dimers has been reported [22]; however, it would seem that the head-to-tail arrangement is favored presumably in part for steric reasons [23]. On the basis of our results, dimerization might account (at least in part) for the photo decay of the alkyl derivatives, but the activity of BHT suggests that the bis(triphenylsilyl)anthracene decays via a different mechanism, possibly involving free radicals. Thus, it might be expected that some reduction of the rate of photo decay would be found for the alkylsilyl systems in a rigid polymer matrix; this might not necessarily be the case for the triphenylsilyl-based system. Some selected studies for polymer films are discussed below.

2.6. Photodecomposition in Polymer Films

2.6.1. Poly(methyl methacrylate). A polymethyl methacrylate (PMMA) film was prepared by dissolving the polymer in dichloromethane (DCM), containing the 9,10-bis(triethylsilyl)anthracene, followed by casting on a glass plate and evaporating to dryness. A similar film was prepared under an argon atmosphere using a glove bag. The films were removed from glass plates once dried and placed under UV light, and their decay was measured at regular intervals; the results are shown in Table 5. As Table 5 shows, the rates of photodegradation are substantially reduced, by an order of magnitude, presumably due to lower rates of diffusion in the

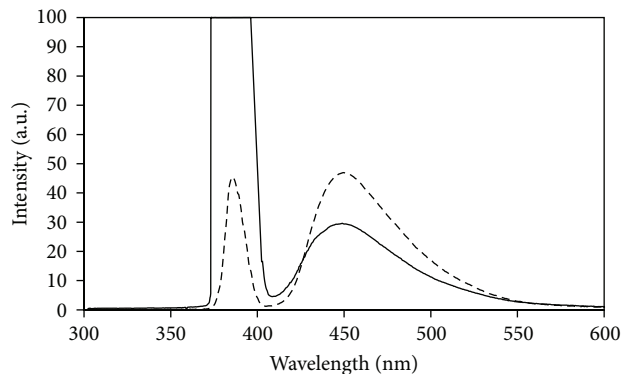


FIGURE 3: Fluorescence spectra of polyacrylonitrile/9,10-bis(triethylsilyl)anthracene film (dashed line) before UV (solid line) after UV irradiation of 7 hours (25200 seconds).

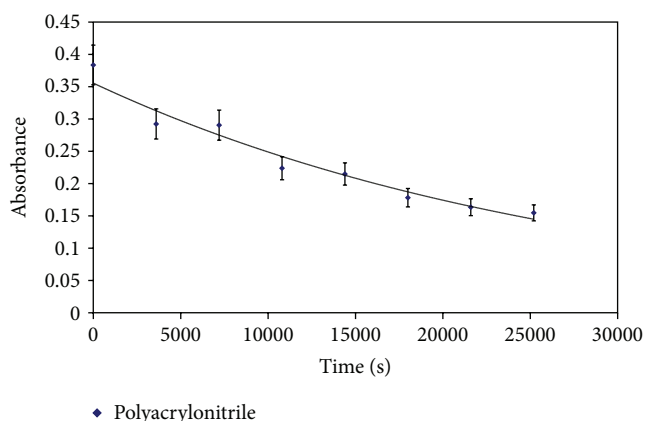


FIGURE 4: Change of absorbance with time for 9,10-bis(triethylsilyl)anthracene in polyacrylonitrile film under UV light; first-order plots suggest a half-life of *ca.* 20,000 s.

polymer matrix. However, here the effect of oxygen seems significantly greater than observed in the solutions, possibly as alternative routes are prevented by encapsulation.

2.7. Comparison of Photostability Studies of 9,10-Bis(trimethylsilyl)anthracene with the Use of Polyacrylonitrile and Polyethylene Films

2.7.1. Polyacrylonitrile. A polyacrylonitrile film was prepared by dissolving the polymer in DMF and incorporating 9,10-bis(triethylsilyl)anthracene, followed by evaporation. UV/visible and fluorescence spectra of the film were obtained before and after irradiation. UV irradiation of the film continued for 7 hours (Figure 4) until the UV spectral readings were too low to measure. The fluorescence spectra obtained following this irradiation are shown in Figure 3 together with the initial spectrum. The film that was used during this experiment turned from purple to colorless which indicated the loss of fluorescence; whilst it was impossible to accurately quantify the fluorescence spectra in the system used here, it would appear that the spectrum is reduced in line with the decrease in absorbance.

TABLE 6: Stability of 9,10-bis(triethylsilyl)anthracene to UV light in polyacrylonitrile and in polyethylene.

Polymer film	Rate constant k (s^{-1})	Half-life ($T_{1/2}$) seconds
Polyacrylonitrile	3.6×10^{-5}	19440
Polyethylene	9.8×10^{-5}	7050

TABLE 7: The photodegradation of 9,10-bis(triphenylsilyl)/ethylsilyl anthracene in sunlight in PMMA.

Day	Absorbance of phenylsilyl film	Absorbance of phenylsilyl film with BHT	Absorbance of ethylsilyl film	Absorbance of ethylsilyl film with BHT
0	0.93	1.67	2.50	2.36
3	0.23	0.69	0.26	0.87
6	0.16	0.4	0.21	0.71

2.7.2. Polyethylene. A polyethylene (LDPE) film was prepared by dissolving the polymer in warm DCM and incorporating 9,10-bis(triethylsilyl)anthracene. The solution was cast onto a glass layer while the warm solvent evaporated. The UV/visible and fluorescence spectra of the film were obtained prior to irradiating with UV light and at various times after irradiation commenced. In this case, the irradiation of the film continued for 210 minutes till the UV/visible spectral readings became difficult to measure accurately, and at the end of 210-minute period both UV and fluorescence spectra were recorded and compared. As for the polyacrylonitrile film, the final fluorescence was much reduced and in line with expectations based on the decrease in absorbance. The results for the chromophore stability in the films are listed in Table 6. As can be seen 9,10-bis(triethylsilyl)anthracene is substantially more stable in polyacrylonitrile than it is in polyethylene, although poly(methyl methacrylate) seemed to be the most effective polymer in terms of increasing stability.

2.8. Comparison of Photostability Studies of 9,10-Bis(triethylsilyl)/(triphenylsilyl) Anthracene in Sunlight with the Use of PMMA Films. On the basis of the photostabilities listed above, the stability of PMMA films containing either bis(triethylsilyl) or bis(triphenylsilyl)anthracenes was tested in sunlight over a period of 6 days in the absence and presence of BHT (carried out in August and in sunny days continuously). The results are summarized in Table 7. As inspection of Table 7 shows, neither film exhibited stability levels in excess of those predicted on the basis of the comparative measurements from the commercial fluorescent material. A particularly surprising feature of this is that when account is taken for the length of day, exposure to sunlight was broadly comparable to the effect of the film being placed 15 cm from a medium pressure UV lamp; this suggests that additional factors such as exposure to moisture and changes in temperature also influence the stability of the chromophores. Although 9,10-bis(triphenylsilyl)anthracene appeared marginally more stable than bis(triethylsilyl)anthracene with estimated half-lives 2.35 (203040 s) days for the former and 1.73 (149472 s) for the latter, this is not in line with the solution studies and



FIGURE 5: Horticultural tunnels undergoing field trials at the University of Reading; the light purple colored films contain stabilized optical brighteners.

once again suggests that there are nonphotochemical routes to the decay of the triphenyl-based chromophores. On a more promising note, addition of BHT increased the stability, even for the triethylsilyl chromophore, where the effect had been much less marked in solution.

3. Conclusion

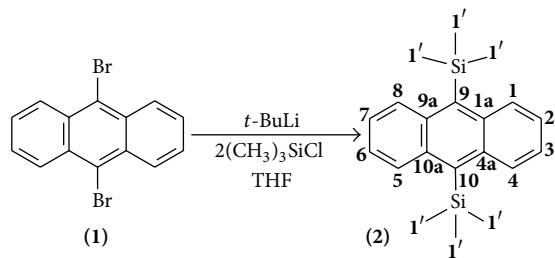
In conclusion 9,10-bis(trialkylsilyl)/triphenylsilyl)anthracene systems have been investigated by synthesizing the numbers of 9,10-disilylalkyl substituted anthracenes and 9,10-bis(triphenylsilyl)anthracene. The compounds have been characterised by various photostability tests followed by calculating their rate constants (k) for photo decay and half-lives ($T_{1/2}$). The materials were tested for their photostability both in solution and various polymer films. It was found during these tests that materials incorporating physical quenching agents had a slightly improved stability. However, sterically hindered structures are more stable resulting in somewhat increased half-lives.

The stability of chromophores dissolved in polymer films was somewhat increased, with rates of decomposition varying with different polymers; here removal of oxygen significantly increased stability. In terms of potential applications, this indicates that films on the inside of glass houses should exhibit improved stability.

In terms of potential application, only the 9,10-bis(triphenylsilyl)anthracene showed comparable UV stability relative to some of the commercially available chromophores tested. Unfortunately this compound was not sufficiently thermally stable for the targeted application. That being said, the stabilization effects shown by the additives discussed above allowed substantial lifetime improvements in films prepared with the commercial chromophores allowing both in field testing (Figure 5) and commercial trials.

4. Experimental Section

All chemicals used during this research were purchased from Aldrich, BDH, Lancaster synthesis, and Acros chemicals and were used as supplied, unless stated otherwise. All solvents used during reactions, workups, and purification



SCHEME 2

procedures were used as supplied, unless stated otherwise. Solvent purification and drying procedures were generally adopted from the books by Perrin and Armarego [24] and Casey et al. [25] as detailed.

4.1. Deoxygenation Technique for Spectral and Photostability Analysis. Deoxygenation was achieved by the use of Freeze-Pump-Thaw and Purging methods as described by Perrin and Armarego [24].

4.1.1. Measuring Photostability of Chromophores in Solution and Polymer Films. Photostability measurements for chromophores were carried out both in solution and polymer films. The chromophores were dissolved in solvent (hexane or DCM 10 mg in 10 mL) and placed in 1 cm \times 1 cm UV cells, subsequently irradiated using the unfiltered radiation from a medium pressure mercury arc lamp (340 nm). The UV absorption of the solutions was measured at regular intervals until the absorption could no longer be accurately measured.

Appropriate polymer films were synthesized by dissolving the chromophores *ca.* 2.5 mg (either with or without the physical quenching agent) in solvent and cast on a glass surface followed by evaporation in the fume hood. The polymer films were subsequently measured for their UV absorption by using the unfiltered radiation from a medium pressure mercury arc lamp (340 nm) at regular intervals until the absorption could no longer be accurately measured. Similarly such polymer films were placed outdoors and exposed to direct sunlight and measured for their UV absorption regularly during the month of August on continuous sunny conditions.

4.1.2. Preparation of 9,10-Bis(trimethylsilyl)anthracene (2) [15]. A solution of *t*-butyllithium in pentane (caution! 1.7 M, 20 mL, 34 mmol) was added dropwise to a suspension of 9,10-dibromoanthracene (2.5 g, 7.4 mmol) (1) in THF (25 mL) at -78°C under an argon atmosphere. The solution was left stirring slowly while adding chlorotrimethylsilane (caution! 2.3 g, 21.2 mmol). The mixture was then stirred for three hours and allowed to warm gradually to room temperature. After an hour the mixture was hydrolyzed with aqueous sodium hydrogen carbonate, and the organic layer was separated using a separating funnel. This was followed by further extraction with petroleum ether, and the solution was dried over anhydrous sodium sulfate to remove any traces

of water. The solvent was evaporated, and the residue was passed through a short column of silica gel with hexane as the eluent. The eluted material was recrystallised with a small amount of ethanol to obtain pale yellow crystals of 9,10-bis(trimethylsilyl)anthracene (2) (yield 0.907 g, 36%) (see Scheme 2).

Mp 111–113 $^\circ\text{C}$ (Lit. 115–117 $^\circ\text{C}$)

I.R.; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 772, 841, (Aromatic C–H out of plane), 1251 (Si–CH₃ aliphatic), 1437 (Si–C aromatic), 1677 (C=C aromatic), 2949 (CH aliphatic)

^1H NMR (250 MHz) CDCl_3 δ (ppm): 0.70 (*s*, 18 H, $\text{H}_{1'}$), 7.35–7.40 (*m*, 4 H, $\text{H}_{2,3}$ & $\text{H}_{6,7}$), 8.35–8.40 (*m*, 4 H, $\text{H}_{1,4}$ & $\text{H}_{5,8}$)

^{13}C NMR (60 MHz) CDCl_3 δ (ppm): 4.6 ($\text{C}_{1'}$), 124.7 ($\text{C}_1 \equiv \text{C}_4 \equiv \text{C}_5 \equiv \text{C}_8$), 129.8 ($\text{C}_2 \equiv \text{C}_3 \equiv \text{C}_6 \equiv \text{C}_7$), 136.8 ($\text{C}_9 \equiv \text{C}_{10}$)

UV/vis Spectrum: ($\lambda_{\text{max}}/\text{nm}$ in hexane): 361 (ϵ 6600), 380 (ϵ 10266), 401.9 (ϵ 9466)

m/z (CI): 322.1570 (M^+), (calculated for $\text{C}_{20}\text{H}_{26}\text{Si}_2$ 322.1574), 251.0382 (calculated for $\text{C}_{17}\text{H}_{18}\text{Si}^+$ 250).

4.2. Preparation of 9,10-Bis(triethylsilyl)anthracene

Yield 2.65 g, 53%

Mp 74–76 $^\circ\text{C}$

I.R.; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 726, 756 (=CH aromatic out of plane), 1235 (Si–CH₂-aliphatic), 1439, 1457 (Si–C aromatic), 1516 (C=C), 2871, 2951 (CH aliphatic)

^1H NMR (250 MHz) CDCl_3 δ (ppm): 0.93 (*t*, 18 H, $\text{H}_{2'}$, $J_{2'1'} = 7.5$ Hz), 1.19 (*q*, 12 H, $\text{H}_{1'}$, $J_{1'2'} = 7.5$ Hz), 7.35–7.40 (*m*, 4 H, $\text{H}_{2,3}$ & $\text{H}_{6,7}$), 8.30–8.35 (*m*, 4 H, $\text{H}_{1,4}$ & $\text{H}_{5,8}$)

^{13}C NMR (60 MHz) CDCl_3 δ (ppm): 8.1 ($\text{C}_{1'}$), 8.5 ($\text{C}_{2'}$), 123.6 ($\text{C}_1 \equiv \text{C}_4 \equiv \text{C}_5 \equiv \text{C}_8$), 129.0 ($\text{C}_2 \equiv \text{C}_3 \equiv \text{C}_6 \equiv \text{C}_7$), 137.1 ($\text{C}_9 \equiv \text{C}_{10}$)

UV/vis Spectrum: ($\lambda_{\text{max}}/\text{nm}$ in hexane): 383.2 (ϵ 10714), 406.3 (ϵ 10535)

m/z (CI): 406.2515 (M^+) (calculated for $\text{C}_{26}\text{H}_{38}\text{Si}_2$ 406.2512).

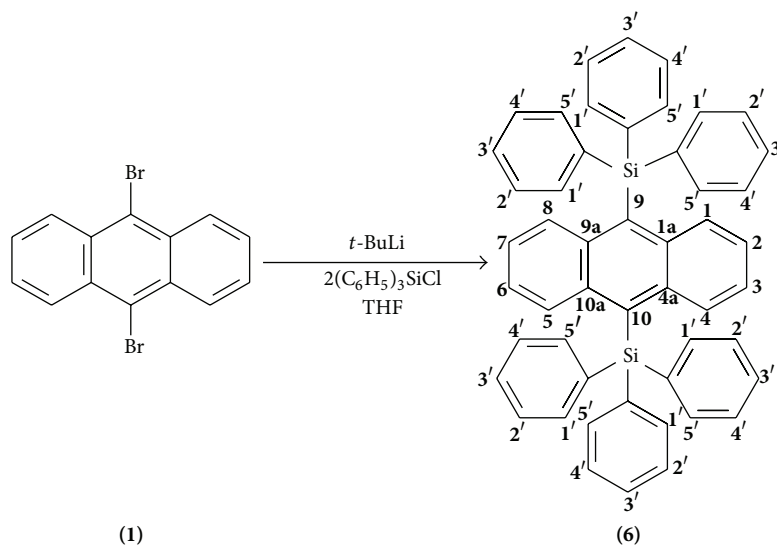
4.3. Preparation of 9,10-Bis(tripropylsilyl)anthracene

Yield 0.407 g, 8%

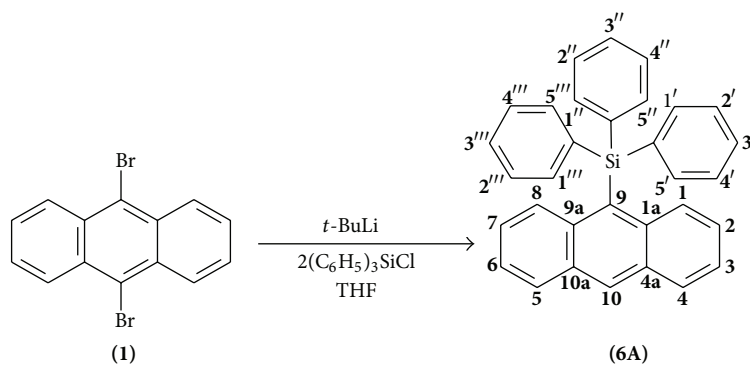
Mp 51 $^\circ\text{C}$

I.R.; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 760 (=CH aromatic out of plane), 1200 (Si–CH₂-aliphatic) 1459 (Si–C aromatic), 1514 (C=C), 2866, 2925 (CH aliphatic)

^1H NMR (250 MHz) CDCl_3 δ (ppm): 0.93 (*t*, 18 H, $\text{H}_{3'}$, $J_{3'2'} = 7.0$ Hz), 1.12–1.20 (*m*, 12 H, $\text{H}_{2'}$), 1.25–1.40 (*m*, 12 H, $\text{H}_{1'}$), 7.35–7.40 (*m*, 4 H, $\text{H}_{2,3}$ & $\text{H}_{6,7}$), 8.30–8.35 (*m*, 4 H, $\text{H}_{1,4}$ & $\text{H}_{5,8}$)



SCHEME 3



SCHEME 4

^{13}C NMR (60 MHz) CDCl_3 δ (ppm): 18.4 ($\text{C}_{1'}$), 18.9 ($\text{C}_{3'}$), 19.9 ($\text{C}_{2'}$), 123.8 ($\text{C}_1 \equiv \text{C}_4 \equiv \text{C}_5 \equiv \text{C}_8$), 129.5 ($\text{C}_2 \equiv \text{C}_3 \equiv \text{C}_6 \equiv \text{C}_7$), 137.5 ($\text{C}_9 \equiv \text{C}_{10}$)

UV/vis Spectrum: (λ_{max} /nm in hexane): 385.4 (ϵ 12150), 406.9 (ϵ 12000)

m/z (CI): 490.3440 (M^+) (calculated for $\text{C}_{32}\text{H}_{50}\text{Si}_2$ 490.3451).

^{13}C NMR (60 MHz) CDCl_3 δ (ppm): 14.1 ($\text{C}_{4'}$), 16.8 ($\text{C}_{1'}$), 26.9 ($\text{C}_{2'}$), 27.1 ($\text{C}_{3'}$), 123.8 ($\text{C}_1 \equiv \text{C}_4 \equiv \text{C}_5 \equiv \text{C}_8$), 129.5 ($\text{C}_2 \equiv \text{C}_3 \equiv \text{C}_6 \equiv \text{C}_7$) 137.5 ($\text{C}_9 \equiv \text{C}_{10}$)

UV/vis Spectrum: (λ_{max} /nm in hexane): 385.9 (ϵ 11666), 407.6 (ϵ 11611)

m/z (CI): 574.4388 (M^+) (calculated for $\text{C}_{38}\text{H}_{62}\text{Si}_2$ 574.4390).

4.4. Preparation of 9,10-Bis(tributylsilyl)anthracene

Yield 0.568 g, 11%

Mp 31°C

I.R.; γ_{max} /cm $^{-1}$ (KBr): 703, 755 (=CH aromatic out of plane), 1296 (Si-CH $_2$ -aliphatic), 1464 (Si-C aromatic), 2869, 2924, 2955 (CH aliphatic)

^1H NMR (250 MHz) CDCl_3 δ (ppm): 0.92 (t , 18 H, $\text{H}_{4'}$, $J_{4'3'} = 7.0$ Hz), 1.12–1.20 (m , 12 H, $\text{H}_{3'}$), 1.21–1.30 (m , 12 H, $\text{H}_{2'}$), 1.30–1.40 (m , 12 H, $\text{H}_{1'}$), 7.35–7.40 (m , 4 H, $\text{H}_{2,3}$ & $\text{H}_{6,7}$), 8.30–8.35 (m , 4 H, $\text{H}_{1,4}$ & $\text{H}_{5,8}$)

4.4.1. Preparation of 9,10-Bis(triphenylsilyl)anthracene (6).

Under an argon atmosphere, a solution of *t*-butyllithium in pentane (caution! 1.7 M, 20 mL, 34 mmol) was added dropwise to a stirred suspension of 9,10-dibromoanthracene (2.5 g, 7.4 mmol) (1) in THF (25 mL) at -78°C . A separate flask solid chlorotriphenylsilane (caution! 4.57 g, 15.5 mmol) (chlorotriphenylsilane recrystallised from a minimum of DCM followed by vacuum drying) was added and dissolved in THF (20 mL), under argon. This solution was then slowly transferred to the 9,10-dibromoanthracene flask by a syringe. The reaction was terminated once the product appeared monitoring by TLC. Upon the workup, the TLC showed

two fluorescing spots *ca.* $R_f = 0.1$ difference. The products were isolated by silica gel column chromatography with hexane as the eluent. The first product isolated was the *mono*-substituted (**6A**) and the second was the *di*-substituted triphenylsilyl anthracene (**6**). The following spectral data are for the *di*-substituted triphenylsilyl anthracene (see Scheme 3).

Yield 0.08 g (<1%)

Mp 260°C (decom.) (Lit. 108°C) [14]

I.R.; $\nu_{\max}/\text{cm}^{-1}$ (KBr): 701, 739 (=CH aromatic out of plane), 1429 (Si-C aromatic)

^1H NMR (250 MHz) CDCl_3 δ (ppm): 6.75–6.80 (*m*, 4 H, $\text{H}_{2,3}$ & $\text{H}_{6,7}$), 7.25–7.40 (*m*, 18 H, $\text{H}_{2',3'}$ & $\text{H}_{4'}$), 7.60–7.70 (*m*, 12 H, $\text{H}_{1',5'}$), 8.05–8.10 (*m*, 4 H, $\text{H}_{1,4}$ & $\text{H}_{5,8}$)

^{13}C NMR (60 MHz) CDCl_3 δ (ppm): 123.9 ($\text{C}_1 \equiv \text{C}_4 \equiv \text{C}_5 \equiv \text{C}_8$), 128.2 ($\text{C}_{2'} \equiv \text{C}_{4'}$), 128.4 ($\text{C}_{3'}$), 130.9 ($\text{C}_2 \equiv \text{C}_3 \equiv \text{C}_6 \equiv \text{C}_7$), 136.6 ($\text{C}_{1'} \equiv \text{C}_{5'}$), 137.5 ($\text{C}_9 \equiv \text{C}_{10}$)

UV/vis Spectrum: (λ_{\max}/nm in hexane): 374.15 (ϵ 14666), 392.75 (ϵ 20266), 414.58 (ϵ 20000)

m/z (CI): 694.44 (M^+) (calculated for $\text{C}_{50}\text{H}_{38}\text{Si}_2$ 694.2512), 436.14 (calculated for $\text{C}_{32}\text{H}_{24}\text{Si}^+$ 436).

4.4.2. For the Mono-Substituted 9-Triphenylsilyl Anthracene. See Scheme 4.

^1H NMR (250 MHz) CDCl_3 δ (ppm): 7.0 (*m*, 2H, $\text{H}_{5'}$ & $\text{H}_{1''}$), 7.50–7.25 (*m*, 12 H, $\text{H}_{2,7} = \text{H}_{3,6}$, $\text{H}_{3',3'',3''}$, $\text{H}_{1',1''}$, $\text{H}_{5'',5''}$ & H_{10}), 7.65–7.60 (*m*, 6 H, $\text{H}_{4',4''}$ & $\text{H}_{2',2'',2''}$), 8.10 (*d*, 2H, H_1 & H_8 , $J = 8.5$ Hz), 8.65 (*d*, 2H, H_4 & H_5 , $J = 8.5$ Hz)

m/z (CI): 436.1653 (M^+) (calculated for $\text{C}_{32}\text{H}_{24}\text{Si}$ 436.1647).

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