FULL PAPER   **WILEY-VCH**

An Unprecedented Photochemical Reaction for Anthracene-Containing Derivatives

Jiang-Lin Zhao,[a] Xue-Kai Jiang,[a] Chong Wu,[a] Chuan-Zeng Wang,[a] Xi Zeng,[b] Carl Redshaw,[c] and Takehiko Yamato*[a]

Abstract: A series of anthracene-containing derivatives (**1**, **2**, **3** and **4**) have been synthesized and characterized. The photochemical behaviour of these derivatives have been investigated by ^{1}H NMR spectroscopies. An unprecedented photolysis reaction for anthracene-containing derivatives was firstly observed in the case of anthracenes directly armed with a $-CH_2O-$R group upon UV irradiation. The photolysis reaction process has been demonstrated to be occurred in three steps. Firstly, the anthracene-containing derivatives are converted to the corresponding endoperoxide intermediate upon UV irradiation in the presence of air; and then, the endoperoxide intermediate is decomposed to the corresponding starting compound and 9-anthraldehyde; finally, 9-anthraldehyde is further oxidised to anthraquinone. Additionally, the photolysis reaction of anthracene-containing derivatives is significantly promoted in the presence of a thiaxalix[4]arene platform.

Introduction

Photochemical reactions have found widespread utility in both bio- and polymer science given that the use of light as a "reagent" is considered an ideal external control element for in situ chemical manipulation, *i.e.* it is clean, inexpensive, acts as very invasive switching stimulus and there is no need to add external chemical species.[1] Furthermore, it can be applied remotely and switched on and off as needed.[2] Of the many photochemical reaction systems known, the photochemistry of anthracene-containing derivatives has drawn particular interest.[3] A great number of investigations suggest that there are two kinds of predominant photoreactions based on anthracene-containing derivatives: 1) a cycloaddition of the central ring of the anthracene forming dimerized anthracene-containing derivatives upon UV light irradiation;[3,4] 2) anthracene-containing derivatives can trap singlet oxygen and form

stable endoperoxides upon UV light irradiation.[5] Additionally, the reverse of the above two reactions can be achieved either thermally or by irradiation with deep UV-light (Scheme 1).
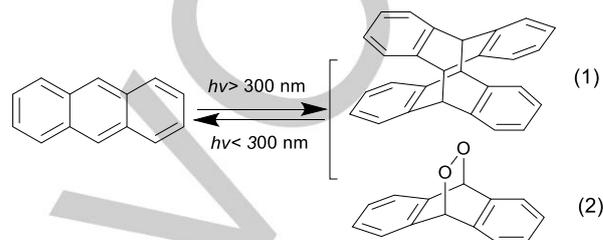
Scheme 1. The reported photochemical reaction.

Herein, we report an unprecedented photochemical reaction for anthracene-containing derivatives based on thiacalix[4]arene. A series of anthracene derivatives (**1**, **2**, **3** and **4**) functionalized at the 9–position has been synthesized, for which the anthracene moiety was employed as the photoactive unit. Further studies showed that the above four compounds underwent favourable decomposition upon UV irradiation following a pathway different to the conventional dimerization or endoperoxide formation. Furthermore, the unexpected photolysis reaction of anthracene-containing derivatives based on thiacalix[4]arene (**1**, **2** and **3**) was significantly promoted in the presence of a thiacalix[4]arene platform. To the best of our knowledge, such a photolyzed photochemical reaction has not been reported previously. We expect that the observed photolysis reaction will provide us a more efficent and convenient protection and deprotection method in thiacalixarene chemistry.

Results and Discussion

Synthesis and characterization

Di-substituted compound **2** could be obtained in 70% yield by the stereoselective *O*-alkylation of compound **1a**[6] with 9-(bromomethyl)anthracene[7] in the presence of Cs_2CO_3 in acetone (Scheme 2). Interestingly, when 9-(bromomethyl)anthracene was replaced by 9-(chloromethyl)-anthracene[8] in this reaction, a mixture of mono-substituted compound **1** and di-substituted compound **2** were obtained even in the presence of a large excess of 9-(chloromethy1)anthracene. This strongly suggested that the stereoselective *O*-alkylation of **1a** was a two-step process. The structures of mono-substituted compound **1** and di-substituted compound **2** were confirmed by ^{1}H NMR, ^{13}C NMR and MS spectra (Figure S5~S10, ESI†). The ^{1}H NMR spectrum of compound **2** exhibited two singlets for the *tert*-butyl protons at

[a] Dr. J.-L. Zhao, Dr. X.-K. Jiang, Dr. C. Wu, Dr. C.-Z. Wang, Dr. Prof. T. Yamato
Department of Applied Chemistry, Faculty of Science and Engineering
Saga University
Honjo-machi 1, Saga 840-8502 Japan
E-mail: yamatot@cc.saga-u.ac.jp
[b] Prof. X. Zeng
Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province
Guizhou University
Guiyang, Guizhou, 550025, China.
[c] Dr. C. Redshaw
Department of Chemistry
The University of Hull
Cottingham Road, Hull, Yorkshire HU6 7RX, UK

supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))
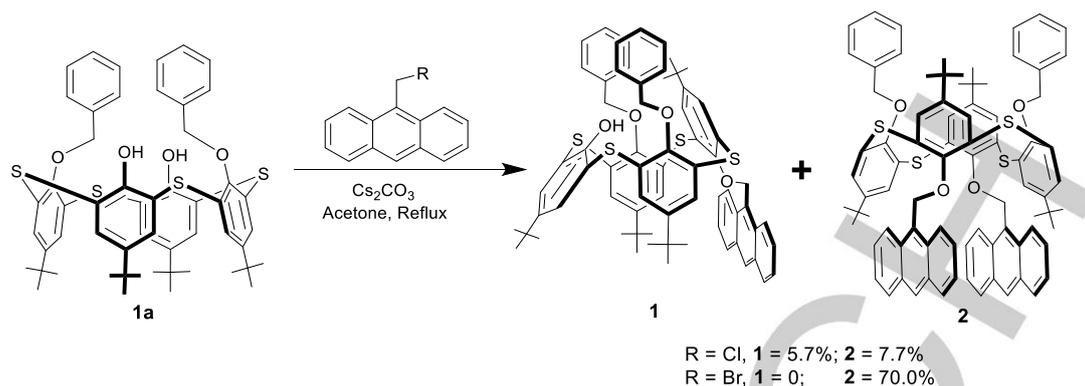
Scheme 2. The synthesis of thiacalix[4]arene derivatives mono-substituted compound **1** and di-substituted compound **2**.

up-field positions, viz δ 0.07 and 0.90 ppm; two singlets for the CH_2 protons at δ 4.95 ppm (OCH_2-Ph) and 5.95 ppm (OCH_2-Anthracene); two singlets for the thiacalix[4]arene aromatic protons at δ 7.07 ppm and 7.38 ppm (Figure S8), all of which was indicative of a C_2-symmmetric di-substituted structure of compound **2** for the 1,3-*alternate* conformation. In contrast, the ^{1}H NMR spectrum of compound **1** showed three singlets for the *tert*-butyl protons (δ 0.36, 0.76 and 1.25 ppm) and the relative intensity was 2: 1: 1, indicating a mono-substituted structure for compound **1** (Fig. S5, see ESI†).

Photochemical reaction studies

The use of ^{1}H NMR spectroscopy allowed the photochemical reaction processes of these anthracene-containing derivatives to be investigated. A 6 mM solution of di-substituted compound **2** in CDCl$_3$ was irradiated by UV light under air. Figure S1 (ESI†) showed the ^{1}H NMR spectra of di-substituted compound **2** under different conditions. In the absence of stimulation, the proton signals at δ = 9.20, 8.48, 7.98, 7.56 and 7.36~7.46 ppm were ascribed to the anthracene moiety of di-substituted compound **2,** and two singlets at δ 4.95 and 5.95 ppm belonged to the linker −CH_2− of di-substituted compound **2** (Detail information in Figure S8, ESI†). Upon irradiation, the intensity of di-substituted compound **2**'s peaks (black coloured peaks, Figure S1, ESI†) gradually diminished with the concomitant appearance of compound mono-substituted compound **1** (peaks at δ = 9.35, 8.52, 8.03, 7.55~7.65 and 7.46~7.53 ppm were ascribed to the anthracene moiety of mono-substituted compound **1**, blue coloured peaks, Figure S1). In other words, di-substituted compound **2** was gradually decomposed to mono-substituted compound **1**. After irradiation for 2 h, all of the peaks which corresponded to compound **1** and **2** had completely disappeared. However, we could not observe the presence of the conventional photodimerization or endoperoxide products, *i.e.* the signal for the bridgehead H_{10} proton of anthracene should be shifted up-field, due to the loss of aromaticity at the central anthracene ring.[3,4,5] Instead, it was replaced by two sets of unexpected new signals: one group of proton signals (δ 5.49, 6.96, 7.32, 7.63, 7.68 and 7.97 ppm, red coloured peaks) which corresponded to the starting compound **1a**[6], and another group of proton signals (δ 7.56, 7.69, 8.08, 8.72, 9.00 and 11.55 ppm, orange coloured peaks) which corresponded to 9-anthraldehyde **5**[9]. All of the observed evidence indicated that the anthracene linker had undergone a cleavage at the middle of anthracene–CH_2O–**1a**; compound **2** had been decomposed by eliminating the

anthracene groups. In other words, an unexpected photolysis reaction was firstly observed in the photochemical reaction of anthracene-containing derivatives. Furthermore, the third group of proton signals (δ 7.80~7.82 and 8.31~8.34 ppm, green coloured peaks) which corresponded to anthraquinone **6**[10] gradually increased upon increasing the irradiation time (1.0 h to 2.0 h). This strongly suggested that the 9-anthraldehyde **5** was further oxidised to the anthraquinone **6**.[11] The proposed photolysis route of anthracene-containing di-substituted compound **2** is shown in Scheme 3. For detail characterization information of the photoproducts, see Figure S17~S21 (ESI†). Similar phenomenon was observed in the case of mono-substituted compound **1** except a shorter photolysis time was required as shown in Figure S2 (ESI†).
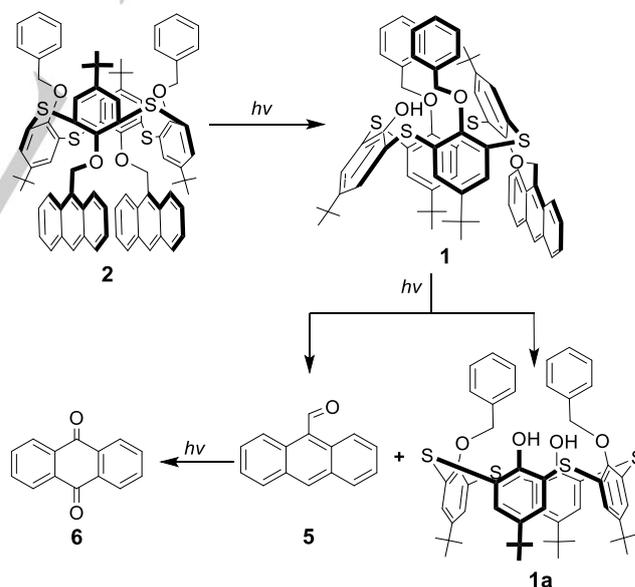
Scheme 3. Proposed photolysis route of compound **2**.

In order to further investigate this rare photolysis phenomenon, compound **3** possessing a similar structure but different substituent (a *di*-ester) in the opposite site was employed (Scheme 4). Interestingly, a totally similar phenomenon was also observed upon the UV irradiation 2 h, such that **3** was decomposed to the corresponding starting compound **3a** and 9-anthraldehyde **5** during the first stage. Subsequently, 9-anthraldehyde **5** was further converted to
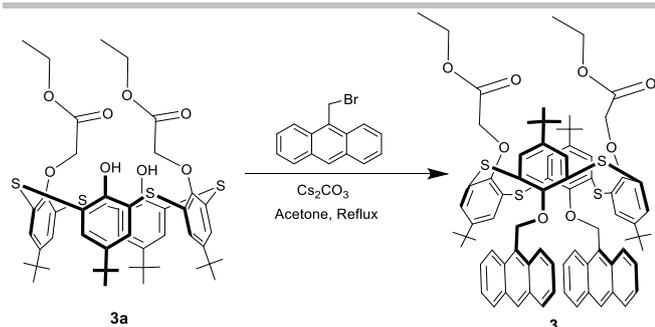
Scheme 4. The synthetic route of thiacalix[4]arene derivative **3**.

anthraquinone **6** during the second stage. The proposed photolysis process of anthracene-containing compound **3** is totally same with compound **1** and **2** (Figure S3, ESI†). Recently, a similar phenomenon was observed by Wirz and coworkers in fluorescein analogues as photoremovable protecting groups. The photoremovable protecting groups was converted to 3,6-dihydroxy-*9H*-xanthen-9-one and 6-hydroxy-3-oxo-*3H*-xanthene-9-carboxylic acid upon irradiation at ~520 nm about 24h.[16] Consequently, it prompted us to propose that the anthracene group can also be acted as a photoremovable protection group and more efficient (~2 hour).

Furthermore, the photolysis reaction prerequisites were discussed. According to our recent work[12a] and that of others[12b,c,d,e], such as the anthracene-containing derivatives (**R1,R2**, **R3**, **R4** and **R5**, Figure 1) bearing different linkers between the anthracene moiety and a thiacalix[4]arene or other platform only gave the conventional photodimerization or endoperoxide photo-products upon UV irradiation. To the best of our knowledge, there are no reports relating to such a
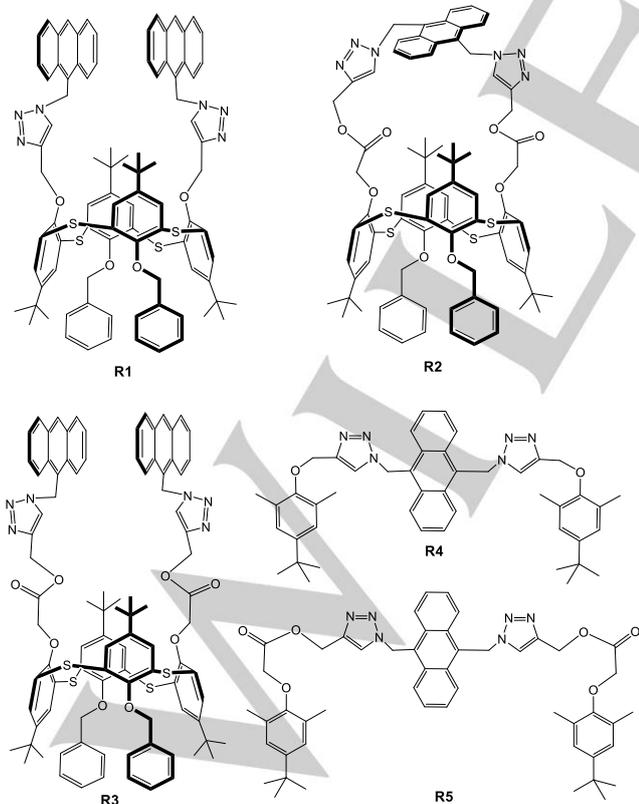
photolyzable photochemical phenomenon based on anthracene-containing derivatives as observed herein. It noteworthy to point out that the only difference between compounds **1**, **2**, **3** and the other reported anthracene-containing compounds is the linker between anthracene moiety and R platform. This strongly suggested that the anthracene–*CH₂O*–R structure played an important role during the photo-decomposition. The photolysis behaviour only occurred in the case of anthracene moiety directly armed with an –*CH₂O*–R group.

Reference compound **4**, which was prepared by *O*-alkylation of 4-*tert*-butyl-2,6-dimethylphenol (**4a**)[14] with 9-(bromomethyl)-anthracene in the presence of Cs₂CO₃, was employed to further study the process of this photolysis reaction (Scheme 5). The proton signals of anthracene moiety (δ 7.47–7.51, 8.03, 8.40 and 8.50 ppm) and benzene ring (δ 7.01 ppm) appeared at up-field positions, indicating a π–π interaction between these two moieties for compound **4** to form an efficient shielding effect. As expected, **4** was finally decomposed to the stating compound **4a** and 9-anthraldehyde **5** upon the irradiation. Subsequently, 9-anthraldehyde **5** was further converted to the anthraquinone **6** (Figure S4, ESI†). The only difference between the reference compound **4** and the thiacalix[4]arene anthracene-containing derivatives (**1**, **2** and **3**) was the photodecomposition time. Compounds **2** and **3** took about two hours to complete the photolysis reaction, compound **1** took about one hour given there is one anthracene group in compound **1** (Figure 2a). However, reference compound **4** needed more than five hours to complete the photolysis reaction (Figure 2b). This suggested
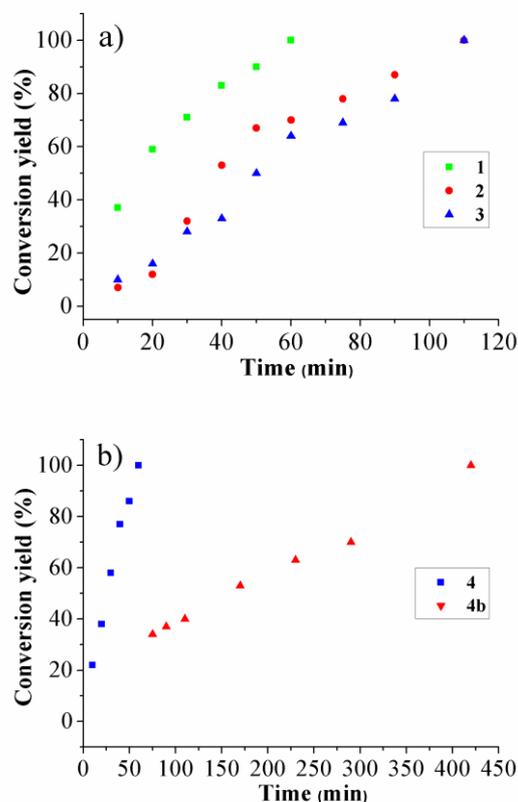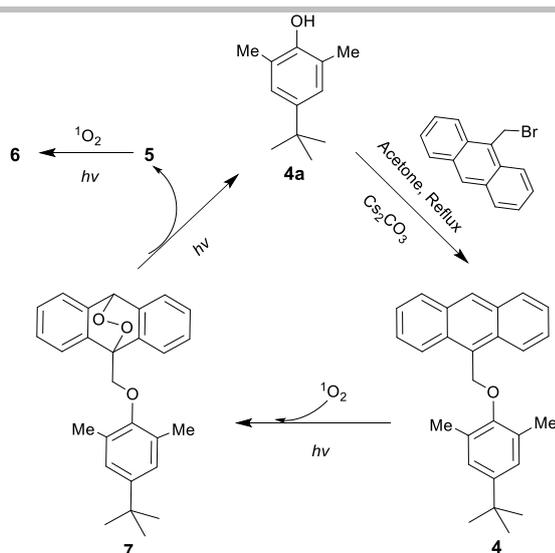

Figure 1. The reported anthracene-containing derivatives.

Figure 2. The conversion yield versus reaction time of a 6 mM CDCl₃ solution of a) **1**, **2** and **3**; b) **4** under irradiation at room temperature.

Scheme 5. Proposed photolysis route of compound **4**.

that the photo-decomposition of the anthracene-containing derivatives was significantly promoted by the presence of a thiaxalix[4]arene platform.

On the other hand, the longer photolysis time of **4** provided us with more information about this photolysis process. Interestingly, when compound **4** was irradiated at the beginning for 1h, it was not directly decomposed, but almost quantitatively initially converted to an intermediate **7** (blue square, Figure 2b and blue peaks, Figure S4, ESI†), and then **7** started to be decomposed to the starting compound **4a** and 9-anthraldehyde **5** (red triangle, Figure 2b and Figure S4, ESI†). Although ^{1}H NMR spectroscopic analysis of the intermediate **7** was possible: δ = 1.26 (9 H, s, *t*-Bu), 1.90 (6 H, s, *CH*₃), 5.69 (1 H, s, *CH*OO), 5.91 (2 H, s, *CH*₂), 6.88 (2 H, s, Ar-*H*), 7.16 (2 H, d, *J* = 7.5 Hz, Anthracene-*H*), 7.25 (2 H, t, *J* = 7.4 Hz, Anthracene-*H*), 7.39 (2 H, t, *J* = 7.5 Hz, Anthracene-*H*) and 7.79 (2 H, d, *J* = 7.8 Hz, Anthracene-*H*) ppm (detail information, Figure S25, ESI†), it was decomposed too quickly to further analysis via ^{13}C NMR or MS spectroscopy. However, when compound **1**, **2**, **3** and **4** was irradiated at 365 nm under an N₂ atmosphere. No detectable changes were observed in the ^{1}H NMR spectra, even after irradiating the compounds for 6 h. Subsequently, comparison with reported results,[3,4,5] prompted us to propose a [4 + 2] cycloaddition with singlet oxygen in this system during the first stage. The [4 + 2] photosensitized oxygenation involving the cycloaddition of ^{1}O₂ (singlet oxygen, an excited state of molecular oxygen which was generated from ambient air by directly irradiation with UV–light.)[15] on the electron-rich carbons of the central anthracene ring had occurred. Thus, we proposed the possible structure for this intermediate as the endoperoxide photo-product **7** (Scheme 5). The photolysis reaction rate of reference compound **4** was slow down due to the presence of π–π interaction between anthracene and benzene ring. The opportunity of the cycloaddition of ^{1}O₂ on the electron-rich carbons of the central anthracene ring was decreased. On the other side, the photochemical reaction rate could be greatly enhanced in the presence of thiacalix[4]arene platform because it served as a host to capture oxygen.[12a] Finally, the whole photolysis process was proposed as shown in Scheme 5.

Conclusions

In conclusion, the synthesis of a series of anthracene derivatives (**1**, **2**, **3** and **4**) functionalized at the 9–position is reported, and their photochemical behaviour has been investigated by ^{1}H NMR spectroscopy. We have observed that a rare photolysis reaction of anthracene-containing derivatives occurred in the case of anthracenes directly armed with a −*CH*₂O–R group upon UV irradiation. Furthermore, the photolysis process has been demonstrated to occur in three steps. Firstly, the anthracene-containing derivatives are converted to the endoperoxide intermediate upon UV irradiation in the presence of air; and then, the endoperoxide intermediate is decomposed to the corresponding starting compound and 9-anthraldehyde; finally, 9-anthraldehyde is further oxidised to anthraquinone. Additionally, the photolysis reaction of anthracene-containing derivatives is significantly promoted in the presence of a thiaxalix[4]arene platform.

Fast (~ 2 hours), clean (light as "reagent") and controllable (irradiation can be switched at will) are the favourable features associated with this photolysis process. It has the practical applications as a protection and deprotection method in the thiacalixarene chemistry to introduce different substituents or construct, such as A, B, C, D systems. Current studies are aimed at exploiting this reaction.

Experimental Section

General procedures

Unless otherwise stated, all reagents used were purchased from commercial sources and were used without further purification. All solvents used were dried and distilled by the usual procedures prior to use. All melting points (Yanagimoto MP-S1) are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian-400MR-vnmrs 400 with SiMe₄ as an internal reference: *J*-values are given in Hz. Mass spectra were obtained with a Nippon Denshi JMS-HX110A Ultrahigh Performance mass spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed by Yanaco MT-5. UV-vis spectra were recorded using a Shimadzu UV-3150UV-vis-NIR spectrophotometer.

Materials

Compound **1a**,[6a] compound **3a**,[13] compound **4a**,[14] 9-(chloromethy1)anthracene[8] and 9-(bromomethyl)anthracene[7] were prepared following the reported procedures..

Synthesis of thiacalix[4]arene derivative (1 and 2).

A mixture of **1a** (200 mg, 0.221 mmol) and Cs₂CO₃ (720 mg, 2.21 mmol) in dry acetone (30 mL) was heated at reflux for 1 h under Ar. Then 9-(chloromethy1)anthracene (501 mg, 2.21 mmol) was added, and the mixture was heated at reflux for 17 h. The resulting solution was cooled and diluted with water and extracted with CHCl₃. The organic layer was separated and dried (MgSO₄) and condensed under reduced pressure to give a yellow solid. The residue was purified by column chromatography (CH₂Cl₂ : haxane = 1:5 to 1:3), gave the desired products **1** (16 mg, 5.7%) and **2** (22 mg, 7.7%) as colourless prisms.

1,3-alternate-25,27-Dibenzyloxy-26-(anthrylmethyl)oxy-28-hydroxy-5, 11,17,23- tetra-tert-butyl-2,8,14,20-tetrathiacalix[4]arene (1): mp 249–250 °C; ^{1}H NMR (400 MHz, CDCl₃) δ 0.36 (18 H, s, *t*Bu), 0.76 (9 H, s, *t*Bu), 1.25 (9 H, s, *t*Bu), 4.87 (2 H, d, *J* = 10.6 Hz, O*CH*₂-Ph), 5.31 (2 H, d, *J* = 10.5 Hz, O*CH*₂-Ph), 6.10 (2 H, s, O*CH*₂- Anthryl), 6.83 (2 H, d, *J* = 2.4 Hz, Ar-*H*), 7.02 (1 H, s, OH), 7.13 (2 H, d, *J* = 2.4 Hz, Ar-*H*), 7.30–7.41 (6 H, m, Ph-*H*), 7.50 (2 H, s, Ar-*H*), 7.46–7.53 (2 H, m, Anthryl-*H*), 7.58 (2 H, s, Ar-*H*), 7.55–7.65 (6 H, m, Anthryl -*H and* Ph-*H*), 8.03 (2 H, d, *J* = 8.3

Hz, Anthryl-*H*), 8.52 (1 H, s, Anthryl-*H*), 9.35 (2 H, d, *J* = 8.9 Hz, Anthryl-*H*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 30.4, 30.5, 31.4, 33.5, 33.6, 34.0, 69.4, 121.8, 125.0, 126.1, 126.5, 127.9, 128.0, 128.1, 128.3, 128.5, 128.5, 128.9, 128.9, 131.6, 133.3, 133.6, 133.7, 136.0, 137.1, 141.9, 146.1, 146.8, 155.8, 157.4, 159.4 ppm; FABMS *m/z* [M+H]$^+$ Calcd for C$_{69}$H$_{71}$O$_4$S$_4$ (1091.4); Found 1091.3. Elemental Anal. Calcd for C$_{69}$H$_{70}$O$_4$S$_4$·H$_2$O: C, 74.69%; H, 6.54%. Found: C, 75.09%; H, 6.42%.

A similar procedure using 9-(bromomethyl)anthracene was followed for the synthesis of product **2** (198mg, 70%).

1,3-alternate-25,27-Dibenzyloxy-26,28-bis[(anthrylmethyl)oxy]-5,11, 17,23-tetra- tert-butyl-2,8,14,20-tetrathiacalix[4]arene (2): mp 253–254°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.07 (18 H, s, *t*Bu), 0.90 (18 H, s, *t*Bu), 4.95 (4 H, s, O*CH$_2$*-Ph), 5.95 (4 H, s, O*CH$_2$*- Anthryl), 7.07 (4 H, s, Ar-*H*), 7.38 (4 H, s, Ar-*H*), 7.36 ~ 7.46 (10 H, m, Ph-*H* & Anthryl-*H*), 7.56 (4 H, t, *J* = 8.0 Hz Anthryl-*H*), 7.65 (4 H, d, *J* = 6.9 Hz, Ph-*H*), 7.98 (4 H, d, *J* = 8.4 Hz, Anthryl-*H*), 8.48 (2 H, s, Anthryl-*H*), 9.20 (4 H, d, *J* = 8.9 Hz, Anthryl-*H*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 30.2, 31.1, 33.2, 33.8, 68.8, 75.3, 124.9, 126.0, 126.3, 127.8, 128.0, 128.2, 128.4, 128.8, 128.9, 129.1, 129.3, 131.5, 131.9, 134.7, 134.8, 137.9, 145.3, 159.5, 159.6 ppm; FABMS: *m/z*: [M+H]$^+$ Calcd for C$_{84}$H$_{81}$O$_4$S$_4$ (1281.5); Found 1281.4. Elemental Anal. Calcd for C$_{84}$H$_{80}$O$_4$S$_4$·2H$_2$O: C 76.56, H 6.42%. Found: C, 76.23, H, 6.00%

Synthesis of thiacalix[4]arene derivative (3).

A mixture of **3a** (1.00 g, 1.12 mmol) and Cs$_2$CO$_3$ (3.65 g, 11.20 mmol) in dry acetone (150 mL) was heated at reflux for 1 h under Ar. Then 9-(bromomethyl)anthracene (0.91 g, 3.36 mmol) was added and the mixture heated at reflux for an additional 24 h. The resulting solution was cooled and diluted with water and extracted with CH$_2$Cl$_2$. The organic layer was separated and dried (MgSO$_4$) and condensed under reduced pressure to give a yellow solid. The residue was purified by column chromatography (CHCl$_3$) to afford the desired product **3** (1.18 g, 83%) as a yellow powder.

1,3-alternate-25,27-Bis[(ethoxycarbonyl)methoxy]-26,28-bis[(anthryl-methyl)oxy]-5,11,17,23–tetra-tert-butyl-2,8,14,20-tetrathiacalix[4]arene (3): mp 248–251°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.05 (18 H, s, *t*Bu), 1.32 (18 H, s, *t*Bu), 1.38–1.35 (6 H, m, CH$_2$*CH$_3$*), 4.30 (4 H, q, *J* = 7.1Hz, *CH$_2$*CH$_3$), 4.66 (4 H, s, O*CH$_2$*COO-), 5.94 (4 H, s, O*CH$_2$*-Anthryl), 7.00 (4 H, s, Ar-*H*), 7.42 (4 H, t, *J* = 7.8 Hz, Anthryl-*H*), 7.53 (4 H, t, *J* = 8.4 Hz, Anthryl-*H*), 7.66 (4 H, s, Ar-*H*), 7.96 (4 H, d, *J* = 8.2 Hz, Anthryl-*H*), 8.46 (2 H, s, Anthryl-*H*), 9.16 (4 H, d, *J* = 8.7 Hz, Anthryl-*H*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.3, 30.2, 31.3, 33.2, 34.2, 60.6, 69.1, 69.2, 124.9, 126.0, 126.3, 127.7, 128.3, 128.5, 128.8, 128.9, 131.6, 131.8, 134.2, 135.4, 145.6, 145.9, 158.2, 159.5, 168.1 ppm; FABMS: *m/z* [M]$^+$ Calcd for C$_{78}$H$_{80}$O$_8$S$_4$ (1272.4736); Found 1272.4739. Elemental Anal. Calcd. for C$_{78}$H$_{80}$O$_8$S$_4$·H$_2$O: C, 72.52; H, 6.40%. Found: C, 72.73, H, 6.24%.

Synthesis of reference compound (4).

A mixture of **4a** (178 mg, 1.0 mmol) and Cs$_2$CO$_3$ (1.63 g, 5.0 mmol) in dry acetone (30 mL) was heated at reflux for 1 h under Ar. Then 9-(bromomethyl)anthracene (271 mg, 1.0 mmol) was added and the mixture heated at reflux for an additional 20 h. The resulting solution was cooled and diluted with water and extracted with CH$_2$Cl$_2$. The organic layer was separated and dried (MgSO$_4$) and condensed under reduced pressure to give a yellow solid. The residue was purified by column chromatography (CH$_2$Cl$_2$: hexance = 1:3) to afford the desired product **4** (350 mg, 95%) as a light yellow solid.

9-((4-(tert-Butyl)-2,6-dimethylphenoxy)methyl)anthracene (4): yellow solid, mp 110–111°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.30 (9 H, s, *t*-Bu), 2.23 (6 H, s, *CH$_3$*), 5.87 (2 H, s, O*CH$_2$*-Anthryl), 7.01 (2 H, s, Ar-*H*), 7.47–7.51 (4 H, m, Anthryl-*H*), 8.03 (2 H, d, *J* = 8.1 Hz, Anthryl-*H*), 8.40 (2 H, d, *J* = 8.4 Hz, Anthryl-*H*), 8.50 (1 H, s, Anthryl-*H*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 17.3, 31.5, 34.1, 67.1, 124.5, 125.0, 125.9, 126.1, 128.6, 129.0, 130.2, 131.0, 131.5, 146.5, 154.6 ppm; FABMS: *m/z*: [M-H]$^+$ Calcd for C$_{27}$H$_{27}$O (367.2062); Found 367.2063.

Characterization of photoproducts (*Known compounds*)

25,27-Dibenzyloxy-5,11,17,23-tetra-tert-butyl-2,8,14,20-tetrathia-calix[4]arene-26,28-diol (1a).[6a] colourless prisms, mp 250–252°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.79 (18 H, s, *t*Bu), 1.34 (18 H, s, *t*Bu), 5.49 (4 H, s, O*CH$_2$*Ph), 6.96 (4 H, s, Ar-*H*), 7.32 (6 H, t, *J* = 6.9Hz, Ph-*H*,), 7.63 (4 H, d, *J* = 6.9Hz, Ph-*H*), 7.68(4 H, s, Ar-*H*), 7.97 (2 H, s, *OH*) ppm.

9-Anthraldehyde.[9] yellow solid, mp 114–116°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.56 (2 H, t, *J* = 7.6 Hz), 7.69 (2 H, t, *J* = 7.6 Hz), 8.08 (2 H, d, *J* = 8.4 Hz), 8.72 (1 H, s), 9.00 (2 H, d, *J* = 8.8 Hz), 11.55 (1 H, s, -*CH*O) ppm; ^{13}C NMR (CDCl$_3$) δ 123.5, 125.7, 129.2, 129.3, 131.1, 132.1, 135.3, 193.0 ppm.

Anthraquinone.[10] yellow needles, mp 282–284°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80–7.82 (4 H, m), 8.31–8.34 (4 H, m) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 127.2, 133.6, 134.1, 183.2 ppm.

25,27-Di[(ethoxycarbonyl)methoxy]-5,11,17,23-tetra-tert-butyl-2,8,14,20-tetrathiacalix[4]arene-26,28-diol (3a).[13] colourless prisms, mp 268–269°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.78 (18H, s, *t*Bu), 1.33 (18H, s, *t*Bu), 1.38 (6 H, t, *J* = 7.2Hz, -CH$_2$*CH$_3$*), 4.42 (4 H, q, *J* = 7.1Hz, -*CH$_2$*CH$_3$), 5.29 (4 H, s, -O*CH$_2$*-), 6.92 (4 H, s, Ar-*H*), 7.67 (4 H, s, Ar-*H*), 8.02 (2 H, s, OH) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ14.3, 30.8, 31.5, 34.0, 34.2, 61.3, 70.3, 122.0, 129.1, 132.6, 134.7, 142.7, 148.5, 154.9, 155.7, 169.0 ppm.

4-(tert-Butyl)-2,6-dimethylphenol (4a).[14] ^{1}H NMR (100 MHz, CDCl$_3$) δ 1.28 (9H, s, *t*Bu), 2.24 (6 H, s, *CH$_3$*), 4.45 (1 H, s, *OH*), 6.99 (2 H, s, Ar-*H*) ppm.

9-((4-(tert-Butyl)-2,6-dimethylphenoxy)methyl)-9,10-dihydro-9,10-epidioxyanthracene (7): ^{1}H NMR (100 MHz, CDCl$_3$) δ = 1.26 (9 H, s, *t*Bu), 1.90 (6 H, s, *CH$_3$*), 5.69 (1 H, s, *CH*OO), 5.91 (2 H, s, *CH$_2$*), 6.88 (2 H, s, Ar-*H*), 7.16 (2 H, d, *J* = 7.5 Hz, Anthracene-*H*), 7.24 (2 H, d, *J* = 7.4 Hz, Anthracene-*H*), 7.39 (2 H, t, *J* = 7.5 Hz, Anthracene-*H*), 7.79 (2 H, d, *J* = 7.8 Hz, Anthracene-*H*) ppm.

[1] a) P. K. Kundu, G. L. Olsen, V. Kiss, R. Klajn, *Nat. Commun.* **2014**, 5, 3588; b) S. Chatani, C. J. Kloxin, C. N. Bowman, *Polym. Chem.* **2014**, 5, 2187-2201; c) S. Monti, I. Manet, *Chem. Soc. Rev.* **2014**, 43, 4051-4067; d) D. Habault, H. Zhang, Y. Zhao, *Chem. Soc. Rev.* **2013**, 42, 7244-7256; e) J.-J. Zhang, Q. Zou, H. Tian, *Adv. Mater.* **2013**, 25, 378-399; f) H. Tian, S.-J. Yang, *Chem. Soc. Rev.* **2004**, 33, 85-97; g) J. Zhang, J. Wang, H. Tian, *Mater. Horiz.* **2014**, 1, 169-184.

[2] a) A. P. Goodwin, J. L. Mynar, Y. Z. Ma, G. R. Fleming, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2005**, 127, 9952-9953; b) J. Q. Jiang, X. Tong and Y. Zhao, *J. Am. Chem. Soc.* **2005**, 127, 8290-8291; c) E. Mabrouk, S. Bonneau, L. Jia, D. Cuvelier, M. H. Li, P. Nassoy, *Soft Matter* **2010**, 6, 4863-4875; d) N. Fonima, C. McFearin, M. Sermsakdi, O. Edigin, A. Almutairi, *J. Am. Chem. Soc.* **2010**, 132, 9540-9542.

[3] a) J. M. Aubry, C. Pierlot, J. Rigaudy, R. Schmidt, *Acc. Chem. Res.* **2003**, 36, 668-675; b) M. Klaper, P. Wessig, T. Linker, *Chem. Commun.*, **2016**, 52, 1210-1213; c) A. Tron, H. P. Jacquot de Rouville, A. Ducrot, J.

H. Tucker, M. Baroncini, A. Credi, N. D. McClenaghan, *Chem. Commun.*, **2015**, 51, 2810-2813.

[4] a) J.-F. Xu, Y.-Z. Chen, L.-Z. Wu, C.-H. Tung, Q.-Z. Yang, *Org. Lett.* **2013**, 15, 6148-6151; b) S. V. Radl, M. Roth, M. Gassner, A. Wolfberger, A. Lang, B. Hirschmann, G. Trimmel, W. Kern, T. Griesser, *Eur. Polym. J.* **2014**, 52, 98-104; c) F. Biedermann, I. Ross, O. A. Scherman, *Polym. Chem.* **2014**, 5, 5375-5382.

[5] a) S. K. Pedersen, J. Holmehave, F. H. Blaikie, A. Gollmer, T. Breitenbach, H. H. Jensen, P. R. Ogilby, *J. Org. Chem.* **2014**, 79, 3079-3087; b) X. Li, G. Zhang, H. Ma, D. Zhang, J. Li, D. Zhu, *J. Am. Chem. Soc.* **2004**, 126, 11543-11548; c) A. Lauer, A. L. Dobryakov, S. A. Kovalenko, H. Fidder, K. Heyne, *Phys. Chem. Chem. Phys.* **2011**, 13, 8723-8732.

[6] a) T. Yamato, C. P. Casas, H. Yamamoto, M. R. J. Elsegood, S. H. Dale, C. Redshaw, *J. Incl. Phenom. Macrocycl. Chem.* **2005**, 54, 261-269; b) J.-L. Zhao, H. Tomiyasu, X.-L. Ni, X. Zeng, M. R. J. Elsegood, C. Redshaw, S. Rahman, P. E. Georghiou, S. J. Teat, T. Yamato, *Org. Biomol. Chem.* **2015**, 13, 3476-3483.

[7] J. R. Shah, P. D. Mosier, B. L. Roth, G. E. Kellogg, R. B. Westkaemper, *Bioorg. Med. Chem.* **2009**, 17, 6496-6504.

[8] I. Mallard, D. Landy, N. Bouchemal, S. Fourmentin, *Carbohydr. Res.* **2011**, 346, 35-42.

[9] a) Y. Zhang, X. Jiang, J. -M. Wang, J. -L. Chen, Y. -M. Zhu, *RSC Adv.* **2015**, 5, 17060-17063; b) S. Wu, L. Chen, B. Yin, Y. Li, *Chem. Commun.*, **2015**, 51, 9884-9887.

[10] a) K. B. Somai Magar, L. Xia, Y. R. Lee, *Chem. Commun.* **2015**, 51, 8592-8595; b) G. Urgoitia, R. SanMartin, M. T. Herrero, E. Domínguez, *Chem. Commun.* **2015**, 51, 4799-4802.

[11] a) S. Gao, W. Wang, B. Wang, *Chem. Lett.* **2001**, 30, 48-49; b) P. Natarajan, V. D. Vagicherla, M. T. Vijayan, *Tetrahedron Lett.* **2014**, 55, 5817-5821.

[12] a) J.-L. Zhao, C. Wu, H. Tomiyasu, X. Zeng, M. R. J. Elsegood, C. Redshaw, T. Yamato, *Chem. Asian J.* **2106**, 11, 1606-1612; b) G. Deng, T. Sakaki, Y. Kawahara, S. Shinkai, *Tetrahedron Lett.* **1992**, 33, 2163-2166; c) G. Deng, T. Sakaki, K. Nakashima, S. Shinkai, *Chem. Lett.* **1992**, 21, 1287-1290; d) G. Deng, T. Sakaki, Y. Kawahara, S. Shinkai, *Supramol. Chem.* **1993**, 2, 71-76; e) C. Schafer, R. Eckel, R. Ros, J. Mattay, D. Anselmetti, *J. Am. Chem. Soc.* **2007**, 129, 1488-1489.

[13] M. Lamouchi, E. Jeanneau, R. Chiriac, D. Ceroni, F. Meganem, A. Brioude, A. W. Coleman, C. Desroches, *Tetrahedron Lett.* **2012**, 53, 2088-2090.

[14] U. Svanholm, V. D. Parker, *J. Chem. Soc., Perkin Trans. 1* **1973**, 1, 562-566.

[15] a) W. Fudickar, T. Linker, *Langmuir* **2010**, 26, 4421-4428; b) C. Bratschkov, *Eur. Polym. J.* **2001**, 37, 1145-1149.

[16] P. Šebej, J. Wintner, P. Müller, T. Slanina, J. A. Anshori, L. A. P. Antony, P. Klán, J. Wirz, *J. Org. Chem.* **2013**, 78, 1833−1843.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

An unprecedented photolysis reaction for anthracene-containing derivatives was observed. The reaction prerequisites and the photo-decompositon process for this photolysis reaction have been investigated.
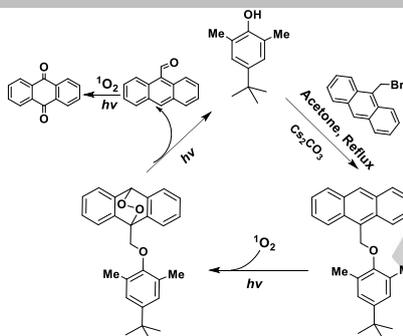
Jiang-Lin Zhao,[a] Xue-Kai Jiang,[a] Chong Wu,[a] Chuan-Zeng Wang,[a] Xi Zeng,[b] Carl Redshaw,[c] and Takehiko Yamato*[a]

Page No. – Page No.

An Unprecedented Photochemical Reaction for Anthracene-Containing Derivatives

Layout 2:

FULL PAPER

((Insert TOC Graphic here; max. width: 11.5 cm; max. height: 2.5 cm))

Author(s), Corresponding Author(s)*

Page No. – Page No.

Title

Text for Table of Contents

Click here to access/download
Supporting Information
2. 0606 Supplementary Information.pdf