A Rare and Exclusive Endoperoxide Photoproduct Derived from Thiacalix[4]arene Crown-shaped Derivative Bearing 9,10–Substituted Anthracene Moiety

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Abstract: A rare and exclusive endoperoxide photoproduct was quantitatively obtained from a thiacalix[4]arene crown-shaped derivative upon irradiation at 365 nm; the structure was unambiguously confirmed by $^{1}H/^{13}C$ NMR spectroscopy and X-ray crystallography. The prerequisites for the formation of endoperoxide photoproduct have also been discussed. Furthermore, 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.

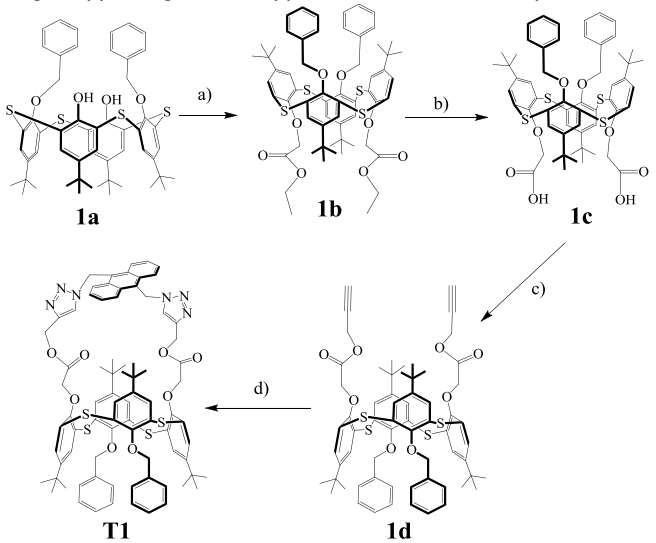
Introduction

Photochemical reactions have found widespread utility in bio- and polymer science given that the use of photons as a "reagent" is considered the least invasive switching stimulus, *i.e.* not requiring addition of any external chemical species.[1] Of the many photochemical reaction systems known, anthracene and its derivatives are of special interest due to the possibility of [4 + 4] reversible photodimerization.[2–5] However, practical applications of this system are limited given that the photochemical reactions are often non-selective, leading to a mixture of products.[3] For example, even in one of the simplest systems, namely the photodimerization of the 9–substituted anthracene derivative, tail–tail and tail–head photoproducts are generated,[2c,4] whilst a multitude of products are isolated in more complex systems.[5] Additionally, it is noteworthy that such photochemical reactions not only form photodimerization products but also endoperoxide products in the presence of oxygen which tend to be overlooked by scientists due to their negligible yield.[6] Indeed, reports relating to the direct characterization of the photoproducts only describe UV absorption spectroscopy to characterize the photoproduct, but in reality this is not rigorous enough.[8] In other words, unambiguous confirmation of the photoproduct is the biggest challenge in a photochemical reaction.

Thiacalix[4]arenes are widely exploited as a molecular platform as the unlimited possibilities for functionalization on the lower-rim, upper-rim and bridging sulfur atoms with various conformations.[9a] Here, we report the synthesis and characterization of a series novel thiacalix[4]arene derivatives (**T1**,**T2** and **T3**) which bear anthracene moiety. Among them, **T1** with 9,10–substituted anthracene group is special interest. The photochemical behaviour of **T1** in solution is described which leads to a rare and exclusive endoperoxide photoproduct. To the best of our knowledge, this is a rare case in which a photoproduct is confirmed unequivocally in macrocyclic chemistry.[9b]

Results and Discussion

The Cu(I)–catalysed azide–alkyne cycloaddition click reaction, was employed to synthesize the novel thiacalix[4]arene crown–shaped derivative **T1** in 36% yield (Scheme 1). As observed in the ^{1}H NMR spectrum of **T1**, the starting proton signal of the propargyl hydrogens of **1d**[10] had disappeared, whilst a new singlet appearing at δ 7.40 ppm was attributed to the protons of



Scheme 1. The synthesis route of thiacalix[4]arene crown-shaped derivative **T1**: a) Cs_2CO_3, 2-bromoethyl acetate, acetone, reflux; b) NaOH, THF:H_2O = 1:1, reflux; c) K_2CO_3, propargyl bromide, acetone, reflux; d) CuI, 9,10-bis(azidomethyl)anthracene, THF:H_2O = 4:1, reflux.

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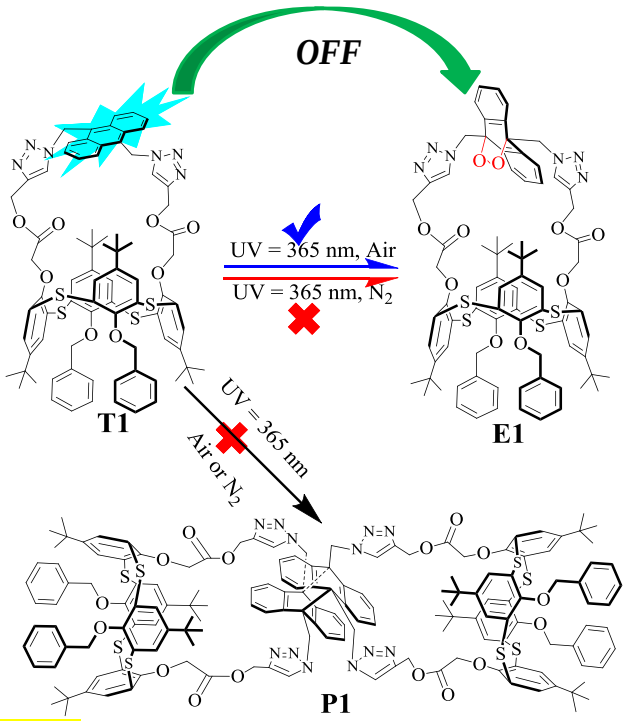


Scheme 2. Two possible photoproduct isomers **E1** and **P1**.

the newly formed triazole skeleton. Two singlets for the *tert*-butyl protons are found unusually up field, *viz* δ 0.79 ppm and 0.30 ppm (due to the additional shielding effect of the anthracene moiety); there are two singlets for the aromatic protons at δ 7.09 and 7.29 ppm, all of which is indicative of a C_2–symmetric structure of **T1** in the 1,3-*alternate* conformation (Figures S1). The target thiacalix[4]arene derivative (**T1**), possessing a crown–shaped thiacalix[4]arene recognition motif functionalized with the anthracene moiety at the 9,10–positions, was employed as the photoactive unit. Use of **T1** had the advantage of limiting the possible number of photoproduct regioisomers to: (i) an intermolecular photodimerization isomer (**P1**) and (ii) an intramolecular endoperoxide isomer (**E1**), see Scheme 2.

The use of ^{1}H NMR spectroscopy allowed the photochemical reaction processes of **T1** (Figure 1) to be investigated. A 6 mM solution of **T1** in $CDCl_3$ was irradiated at 365 nm under air. Upon irradiation, a new group of proton signals (red colour peaks) immediately appeared with a concomitant decrease in the concentration of **T1** (blue colour peaks). An indication of the photochemical reaction process was the signals of the anthracene proton resonances (δ 7.83 and 8.65 ppm) which gradually decreased and finally disappeared. On gradually increasing the irradiation time, the conversion yield gradually increased as expected. After 90 min, the quantitative conversion was indicated by the complete disappearance of all of the **T1** proton resonances, whilst a new unambiguous group of signals appeared. The photoactive anthracene motif resulted in xylene–like units for which proton signals appeared at δ 7.35 ppm and δ 7.58 ppm (for characterization data, see Figure S4, ESI†). The unusually up field *tert*-butyl protons (δ 0.30 ppm) dramatically shifted back to their 'normal' chemical shift position (δ 0.89 ppm)

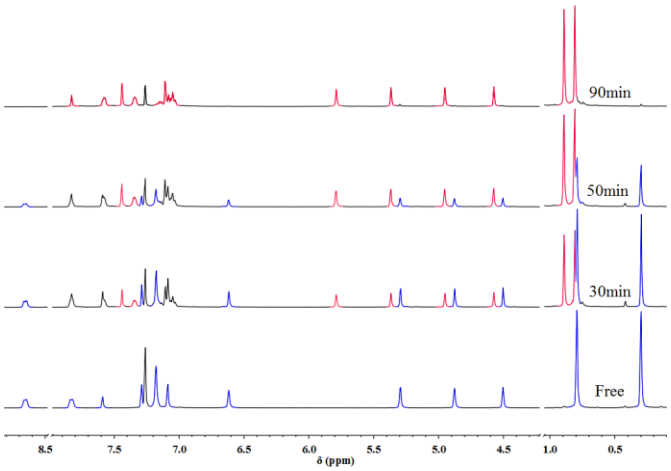


Figure 1. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) spectra of a 6 mM solution of **T1**, after irradiation at 365 nm (0 min, 30 min, 50 min, 90 min).

due to the deshielding effect after the loss of aromaticity of the central anthracene ring.

Another indication of the photochemical process was the appearance of a new peak of the photoproduct at δ 79.7 ppm corresponding to the bridgehead $C_{9,10}$ carbon for the former central anthracene ring in the ^{13}C NMR spectrum (Figure S5, ESI†). The resulting UV absorption spectrum of **T1** after irradiation (Figure 2a) fully supported the formation of planar-symmetric photoproducts involving only the central anthracene ring and not the lateral anthracene aromatic rings, *i.e.* there was no absorption beyond 300 nm.[4a] A similar conclusion can be drawn from fluorescence studies (Figure 2b). The characteristic anthracene moiety emission of **T1** in the 375–525 nm region

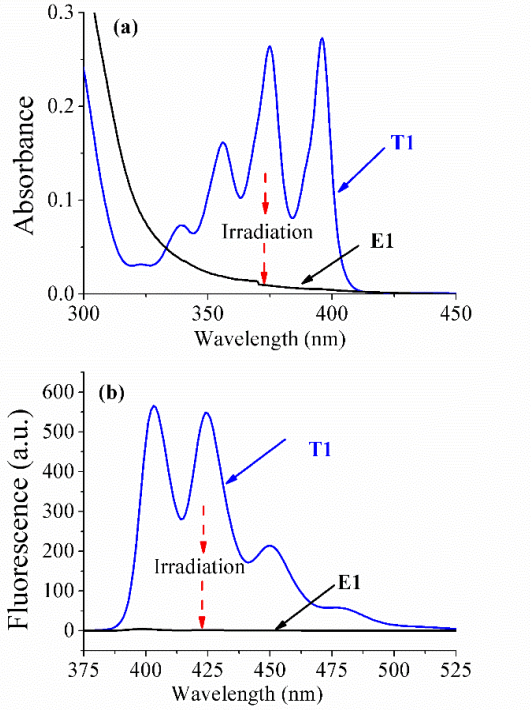


Figure 2. UV-visible spectra (a) and fluorescence spectra (b) of a 2.4 × 10^{-5} M solution of the **T1** in $CHCl_3$ under irradiation.

was switched ‘‘off’’ after irradiation, which mirrored the non-fluorescence photoproduct formation. In contrast, a 6 mM solution of **T1** in degassed $CDCl_3$ was irradiated at 365 nm under an N_2 atmosphere. No detectable changes were observed in the ^1H NMR spectra, even after irradiating the compound for 6 h (Scheme 2).

As mentioned previously, normally the characterization of the photoproduct is the biggest challenge after the photochemical reaction, given the numerous photoproducts possible. Even for our simplest system, there remain two possible photoproduct isomers **E1** and **P1**. Fortunately, the quantitative conversion provided a pure photoproduct which was easily confirmed by mass spectrometry. The observed mass result *m/z* = 1413.4907 $[M + H]^+$ (Figure S6, ESI†) and *m/z* = 1380.4910 $[M]^+$ for unirradiated **T1** (Figure S3, ESI†) strongly suggested that the photoproduct was the endoperoxide photoproduct **E1**. Furthermore, X–ray crystallographic analysis[14] further confirmed the molecular structure of **E1** as shown in Figure 3. $C_{80}H_{80}N_6O_{10}S_4•2(CH_4O)$, one endoperoxide photoproduct **E1** in 1,3-*alternate* conformation and two molecules of methanol were in the asymmetric unit (Figure S7, ESI†). The central anthracene ring moiety of the **T1** molecule has been oxidized rather than linking to another thiacalix[4]arene. These results for **E1** confirmed that the normally [4 + 4] photodimerization reaction had not occurred, but rather an unexpected [4 + 2] photosensitized oxygenation involving the cycloaddition of $^1O_2$ (singlet oxygen, an excited state of molecular oxygen which was generated from ambient air by directly irradiation with UV–light.)[8] on the electron-rich carbons of the central anthracene ring had occurred.[6,7] The most noteworthy feature was the position of the –O10–O9– bond which was oriented inward instead of the normally favorable outward direction, and this may be attributed to the inwardly crown–shaped structure required to trap the singlet oxygen.[9b]

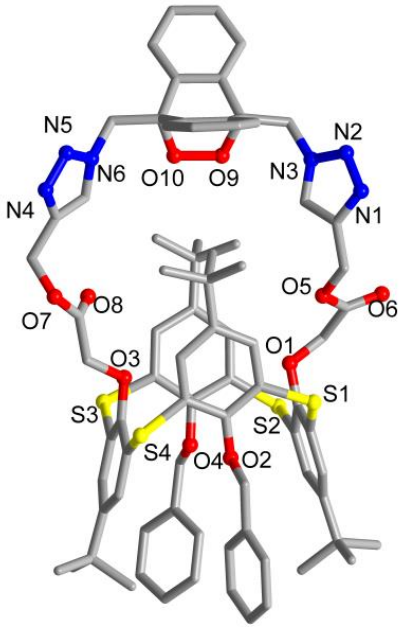
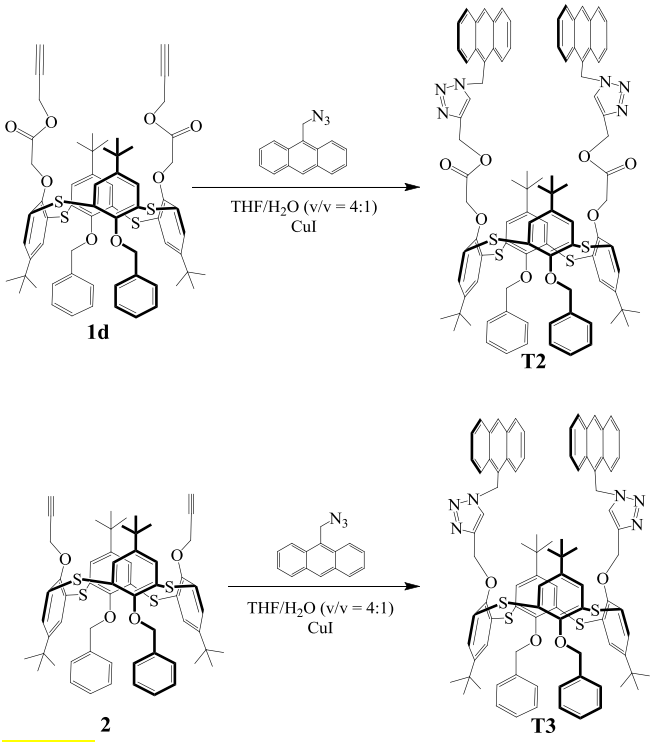


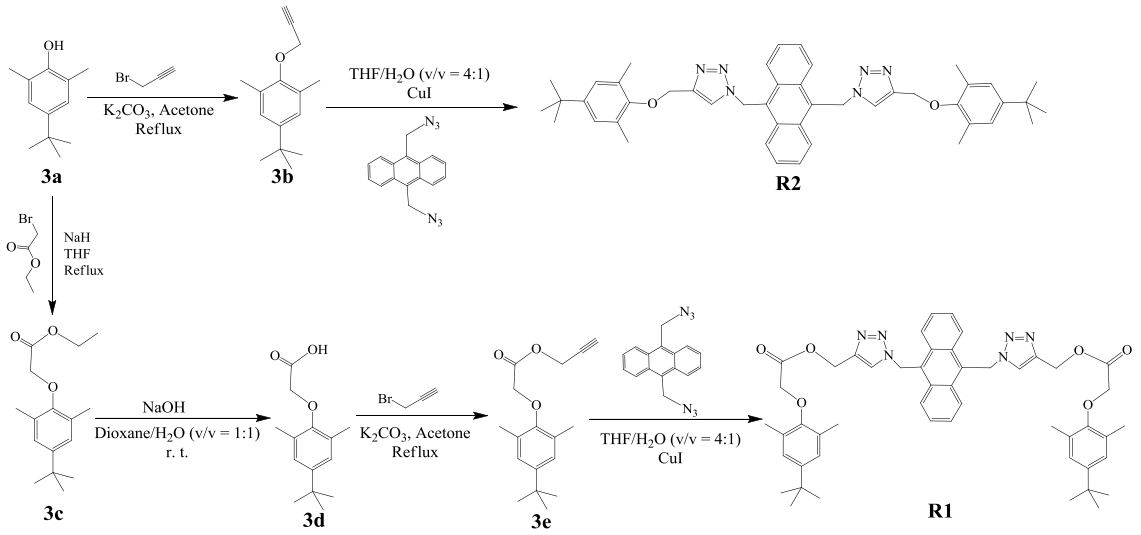
Figure 3. Single-crystal structure of **E1**. Hydrogen atoms and the two methanol molecules of crystallization have been omitted for clarity.



Scheme 3. The synthetic route of thiacalix[4]arene derivatives **T2** and **T3**.

In order to further investigate the rare endoperoxide photochemical phenomenon, **T2** with 9–substituted anthracene moiety as the photoactive unit and **T3** with similar structure but short linkage have been introduced (Scheme 3). Interestingly, no matter UV absorption spectrum or fluorescence spectrum of compound **T2** and **T3** were almost the same with compound **T1** which were quenched after irradiation (Figure S8, ESI†). However, unfortunately, the ^1H NMR spectroscopy were gradually changed to very complicate which could not be used to identified any of the photoproducts when compound **T2** or **T3** was irradiated under the same condition with compound **T1** (Figure S9-S10, ESI†). The observed phenomenon in **T2** and **T3** were similar with most reported results which was crudely defined to photodimerization.[2-8] It strongly suggested that 9,10–substituted anthracene crown–shaped moiety of compound **T1** was the key for the formation of this rare endoperoxide photoproduct.

Furthermore, two reference compounds **R1** and **R2** possessing 9,10–substituted anthracene with different linkages have also been synthesized (Scheme 4). The photochemical reaction processes of **R1** and **R2** have also been investigated by ^1H NMR spectroscopy and UV absorption spectrum. Surprisingly, all of the results were similar with thiacalix[4]arene derivative **T1**. UV absorption spectrum of compound **R1** and **R2** were quenched after irradiation (Figure S11, ESI†); a quantitative conversion was observed by that all of the **R1** or **R2** proton resonances were replaced by a new unambiguous group of signals after irradiation (Figure S12-S13, ESI†). All of the observed results strongly suggested that endoperoxide photoproducts were also formed during these photochemical process of **R1** and **R2**. In other words, the compounds which



Scheme 4. The synthetic route of reference compounds **R1** and **R2**

were possessing 9,10–substituted anthracene in a symmetric structure (RCH_2-Anthracene-CH_2R) was favorable to form the endoperoxide photoproduct rather than dimerization photoproduct. However, more interestingly, we should point out that that However, more interestingly, we should point out that the time it takes to complete the photochemical reactions of **T1**, **R1** and **R2** to corresponding **E1**, **E2**, and **E3** are 90, 140, and 120 min, respectively (Figure 4). It maybe attribute to the thiacalix[4]arene platform can be served as a host to capture oxygen which was conducive to form endperoxide photoproduct. It was consistent with the unique X-ray results, the position of the –O10–O9– bond which was oriented inward instead of the normally favorable outward direction. In other words, the unique thiacalix[4]arene platform could greatly enhance the photochemical reaction rate.

Many studies have pointed out that the decomposition of photoproducts would occur either thermally (~60 °C) or by irradiation with deep UV–light (<300 nm), or would even occur naturally.[2b,11] However, in our case, the thermal cycloreversion of the endoperoxide photoproduct **E1** was also investigated and no change in the ^{1}H NMR spectra was observed, even after heating the compound to 150 °C for 8 h. Another typical cycloreversion method was performed by irradiating the **E1** solution at 254 nm. However, even after 4 h, the UV–vis and ^{1}H NMR spectra also showed no change. These relative photon/thermal stabilities of the photoproduct suggested that the formation of the **E1** photoproduct has been shown to be very stable under these conditions.

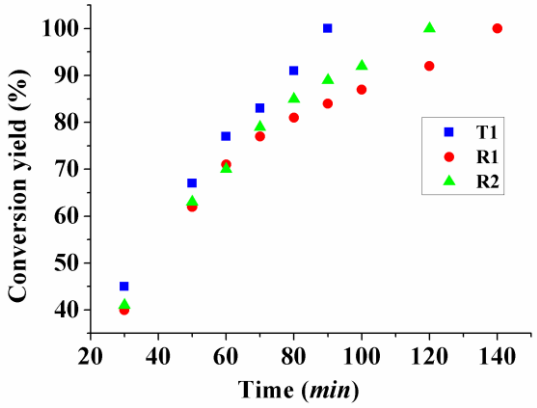


Figure 4. The conversion yield versus reaction time of a 6 mM $CDCl_3$ solution of **T1**, **R1** and **R2** under irradiation at 365 nm.

Singlet oxygen ($^1O_2$) is an excited state of molecular oxygen which has attracted great interest as $^1O_2$ is believed to play an important role in species for organic synthesis, bleaching processes, and most importantly, the photodynamic therapy of cancer, which has now obtained regulatory approval in most countries for the treatment of several types of tumors.[12,13] However, excessive levels of $^1O_2$ can often be toxic to certain biological systems and the technique for detecting $^1O_2$ is still limited due to its short lifetime.[12] Monitoring the direct emission of $^1O_2$ at 1270 nm is the most common method[13c], but such detection is limited by the low sensitivity.[15e] To improve the sensitivity, fluorimetry is the first choices which is rapidly performed, nondestructive and greater sensitivity.[15] Indeed, scientist have successfully designed few fluorescent probes which trapped with $^1O_2$ to give a sensitive fluorescence response.[16] However, designing a suitable $^1O_2$ fluorescent probe is still a big challenge. The modified **T1** with anthracene functionalities allows for a rapid reaction with low concentrations of singlet oxygen $^1O_2$ concomitant with UV–vis and fluorescence spectra changes at room temperature. In other words, the compound **T1** has potential application as a high selectivity and high sensitivity chemosensor for detection of singlet oxygen. Current studies are aimed at exploring **T1** as a practical chemosensor for singlet oxygen.

Conclusions

In summary, the synthesis of a new thiacalix[4]arene crown-shaped derivative **T1** is reported, and the photochemical behaviour has been investigated by ^{1}H NMR, UV–vis and fluorescence spectroscopies. We have demonstrated that the

photochemical reaction of **T1** (bearing anthracene moieties) converts it to the endoperoxide **E1** in quantitative yield upon irradiation at 365 nm. The structure of the rare endoperoxide photoproduct **E1** was unambiguously confirmed by $^{1}H/^{13}C$ NMR spectroscopy and X-ray crystallography. Further studies revealed that the compounds which were possessing 9,10–substituted anthracene in a symmetric structure (RCH_2-Anthracene-CH_2R) were favorable to form the endoperoxide photoproduct rather than dimerization photoproduct. Furthermore, the photochemical reaction rate could be greatly enhanced in the presence of thiacalix[4]arene platform which was attributed to the thiacalix[4]arene platform can be served as a host to capture oxygen.

Experimental Section

General procedures

All melting points (Yanagimoto MP-S1) are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian–400MR–vnmrs400 with $SiMe_4$ 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. UV–vis spectra were recorded using a Shimadzu UV–3150UV–vis–NIR spectrophotometer. Fluorescence spectroscopic studies of compounds in solution were performed in a semimicro fluorescence cell (Hellma®, 104F–QS, 10 × 4 mm, 1400 µL) with a Varian Cary Eclipse spectrophotometer. Irradiation at 365 nm was performed with a UV lamp (AH 400PR, AC 100V, 60 Hz). Irradiation at 254 nm was performed with a 4W TLC UV lamp (ASONE Handy UV Lamp, SLUV-4).

Materials: Unless otherwise stated, all reagents used were purchased from commercial sources and were used without further purification. Compound **1a**[17]**, 1b**[18]**, 1c**[18]**, 1d**[10], **2**[19], **3a**[20], **3c**[21], **3d**[21] and 9–(azidomethyl)anthracene[22] and 9,10–bis(azidomethyl)anthracene[23] were prepared following the reported procedures. All solvents used were dried and distilled by the usual procedures prior to use.

Synthesis of thiacalix[4]arene derivative (T1) Copper iodide (20 mg) was added to a mixture of **1d** (219 mg, 0.20 mmol) and 9,10-bis(azidomethyl)anthracene (70 mg, 0.24 mmol) in 75 mL THF/H_2O (4:1) and refluxed for 15 h. The resulting solution was cooled and diluted with water and extracted with CH_2Cl_2. The organic layer was separated and dried ($MgSO_4$) and evaporated to give the solid crude product. The residue eluted from a column chromatography column of silica gel with CH_2Cl_2/EtOAc (20:1) gave the desired product **T1** (100 mg, 36%) as light yellow powder. M.p. 361–362 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 18H, t*Bu*), 0.79 (s, 18H, t*Bu*), 4.50 (s, 4H, –O*CH*$_2$COO–), 4.88 (s, 4H, –O*CH*$_2$Benzyl), 5.29 (s, 4H, –O*CH*$_2$Triazole–), 6.62 (s, 4H, –Triazole*CH*$_2$An), 7.09 (s, 4H, Ar*H*), 7.18 (s, 10H, Ph*H*), 7.29 (s, 4H, Ar*H*), 7.59 (s, 2H, Triazole–*H*), 7.82–7.84 (m, 4H, An–*H*) and 8.65–8.66 (m, 4H, An–*H*) ppm. ^{13}C NMR (100 MHz) δ 29.8, 30.7, 33.2, 33.8, 47.3, 57.9, 67.0, 73.4, 123.5, 124.6, 127.1, 127.2, 127.4, 127.5, 128.0, 128.2, 128.5, 131.1, 131.2, 133.5, 137.9, 143.6, 145.4, 145.9, 156.9, 158.4 and 168.3 ppm. FABMS: *m/z*: $[M]^+$ Calcd for $C_{80}H_{80}N_6O_8S_4$ 1380.4921; Found 1380.4910.

A similar procedure using **1d**, **2**, **3b** and **3e** was followed for the synthesis of **T2**, **T3**, **R1** and **R2**.

Thiacalix[4]arene derivative (T2) was obtained as a light yellow solid (a column chromatography column of silica gel with hexane/CH_2Cl_2/EtOAc (10:10:1), 104 mg, 48%). M.p. 231–232 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.80 (s, 18H, t*Bu*), 1.01 (s, 18H, t*Bu*), 4.47 (s, 4H, –O*CH*$_2$COO–), 4.91 (s, 4H, –O*CH*$_2$Benzyl), 5.11 (s, 4H, –O*CH*$_2$Triazole–), 6.54 (s, 4H, –Triazole*CH*$_2$An), 7.05 (s, 4H, Ar*H*), 7.18 (s, 10H, Ph*H*), 7.22 (s, 2H, Triazole–*H*), 7.34 (s, 4H, Ar*H*), 7.45– 7.54 (m, 4H, An-*H*), 7.54 – 7.63 (m, 4H, An-*H*), 8.05–8.07 (m, 4H, An-*H*), 8.29–8.31 (m, 4H, An-*H*) and 8.57 (s, 2H, An-*H*) ppm. ^{13}C NMR (100 MHz) δ 30.8, 30.9, 46.5, 57.6, 66.8, 73.1, 122.9, 123.1, 123.5, 125.4, 127.1, 127.4, 127.8, 128.2, 128.5, 129.5, 130.0, 130.80, 130.83, 131.5, 133.0, 138.0, 142.7, 145.9, 146.0, 156.0, 158.2 and 167.6 ppm. FABMS: *m/z*: $[M+H]^+$ Calcd for $C_{94}H_{91}N_6O_8S_4$ 1559.5781; Found 1559.5780.

Thiacalix[4]arene derivative (T3) was obtained as a light yellow solid (a column chromatography column of silica gel with hexane/CH_2Cl_2/EtOAc (20:10:1), 580 mg, 74%). M.p. 284–285 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.60 (s, 18H, t*Bu*), 1.20 (s, 18H, t*Bu*), 4.66 (s, 4H, –O*CH*$_2$Benzyl), 5.03 (s, 4H, –O*CH*$_2$Triazole–), 6.50 (s, 4H, –Triazole*CH*$_2$An), 6.58 (s, 2H, Triazole–*H*), 6.75 (s, 4H, Ar*H*), 7.06–7.07 (m, 4H, Ph*H*), 7.12–7.17 (m, 6H, Ph*H*), 7.47 (s, 4H, Ar*H*), 7.46–7.49 (m, 4H, An-*H*), 7.53–7.56 (m, 4H, An-*H*), 8.01–8.03 (m, 4H, An-*H*), 8.24–8.26 (m, 4H, An-*H*) and 8.51 (s, 2H, An-*H*) ppm. ^{13}C NMR (100 MHz) δ 29.6, 30.3, 32.5, 33.2, 45.3, 61.9, 72.1, 121.9, 122.0, 122.6, 124.3, 125.8, 126.3, 126.6, 127.0, 128.3, 128.7, 128.9, 129.0, 129.8, 130.3, 133.0, 137.1, 142.5, 144.3, 144.9, 154.5 and 157.5 ppm. FABMS: *m/z*: $[M+H]^+$ Calcd for $C_{90}H_{87}N_6O_4S_4$ 1443.5672; Found 1443.5670.

Reference compound (R1) was obtained as a light yellow solid (a column chromatography column of silica gel with CH_2Cl_2/EtOAc (20:1), 260 mg, 57%). M.p. 256–257 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.26 (s, 18H, t*Bu*), 2.13 (s, 12H, *CH*$_3$), 4.29 (s, 4H,–O*CH*$_2$COO), 5.19 (s, 4H, –O*CH*$_2$Triazole–), 6.60 (s, 4H, –Triazole*CH*$_2$An), 6.94 (s, 4H, Ar*H*), 7.32 (s, 2H, Triazole–*H*), 7.67–7.70 (m, 4H, An-*H*) and 8.43–8.46 (m, 4H, An-*H*) ppm. ^{13}C NMR (100 MHz) δ 16.4, 31.4, 34.1, 46.6, 57.9, 68.9, 123.5, 124.1, 125.8, 126.9, 127.8, 129.6, 130.7, 142.6, 147.1, 152.9 and 169.1 ppm. FABMS: *m/z*: $[M+H]^+$ Calcd for $C_{50}H_{57}N_6O_6$ 837.4340; Found 837.4376.

Reference compound (R2) was obtained as a yellow solid (recrystallized from 1:3 $CHCl_3$/hexane, 145 mg, 87%). M.p. 302–303 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.23 (s, 18H, t*Bu*), 2.13 (s, 12H, *CH*$_3$), 4.80 (s, 4H,–O*CH*$_2$Triazole–), 6.63 (s, 4H, –Triazole*CH*$_2$An), 6.91 (s, 4H, Ar*H*), 7.30 (s, 2H, Triazole–*H*), 7.68–7.71 (m, 4H, An-*H*) and 8.48–8.50 (m, 4H, An-*H*) ppm. ^{13}C NMR (100 MHz) δ 16.6, 31.4, 34.1, 46.6, 65.6, 122.1, 124.2, 125.7, 127.1, 127.7, 129.9, 130.7, 145.2, 146.8 and 152.9 ppm. FABMS: *m/z*: $[M+H]^+$ Calcd for $C_{46}H_{53}N_6O_2$ 721.4230; Found 721.4244.

Photoproduct from T1 (**E1**) was obtained as a yellow solid (5 mg, 100%). M.p. 289–290 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.81 (s, 18H, t*Bu*), 0.89 (s, 18H, t*Bu*), 4.57 (s, 4H, –O*CH*$_2$COO–), 4.95 (s, 4H, –O*CH*$_2$Benzyl), 5.37 (s, 4H, –O*CH*$_2$Triazole–), 5.79 (s, 4H, –Triazole*CH*$_2$C), 7.03–7.08 (m, 8 H, Ph*H*), 7.11 (s, 4H, Ar*H*), 7.14~7.17 (m, 2H, Ph*H*), 7.35 (br, 4H, Benzene–*H*), 7.44 (s, 4H, Ar*H*), 7.58 (br, 4H, Benzene–*H*) and 7.83 (s, 2H, Triazole–*H*) ppm. ^{13}C NMR (100 MHz) δ 30.5, 30.7, 33.8, 48.8, 58.5, 66.9, 72. 5, 79.7, 121.4, 126.2, 126.9, 127.0, 127.9, 128.12, 128.15, 128.4, 129.9, 132.5, 137.8, 138.2, 144.0, 145.98, 146.02, 155.8, 158.2 and 168.5 ppm. FABMS: *m/z*: $[M+H]^+$ Calcd for $C_{80}H_{81}N_6O_{10}S_4$ 1413.4897; Found 1413.4907.

Photoproduct from R1 (**E2**) was obtained as a light yellow solid (6 mg, 100%). M.p. 114–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.27 (s, 18H, t*Bu*), 2.22 (s, 12H, *CH*$_3$), 4.39 (s, 4H,–O*CH*$_2$COO), 5.31 (s, 4H, –O*CH*$_2$Triazole–), 5.75 (4 H, s, –Triazole*CH*$_2$C), 6.96 (4 H, s, Ar*H*), , 7.26 (4 H, s, Ph-*H*), 7.43 (s, 4H, Ph-*H*) and 8.00 (s, 2H, Triazole–*H*). ^{13}C NMR (100 MHz) δ 16.5, 31.4, 34.1, 48.7, 57.9, 69.0, 80.0 121.2, 125.9, 126.7,

128.3, 129.7, 137.8, 143.2, 147.0, 153.0 and 169.0 ppm. FABMS: *m/z*: $[M+H]^+$ Calcd for $C_{50}H_{57}N_6O_8$ 869.4238; Found 869.4236.

Photoproduct from R2 (**E3**) was obtained as a light yellow solid (5 mg, 100%). M.p. 128–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.27 (s, 18H, t*Bu*), 2.25 (s, 12H, CH_3), 4.92 (s, 4H,–OCH_2Triazole–), 5.78 (s, 4H, –TriazoleCH_2C), 6.99 (s, 4H, Ar*H*), 7.26–7.27 (m, 4H, Ph-*H*), 7.46–7.48 (m, 4H, Ph-*H*) and 8.00 (s, 2H, Triazole–*H*). ^{13}C NMR (100 MHz) δ 16.7, 31.5, 34.1, 48.7, 65.5, 80.2, 121.3, 125.6, 125.8, 128.3, 130.0, 137.9, 145.7, 146.8 and 153.2 ppm. FABMS: *m/z*: $[M+H]^+$ Calcd for $C_{46}H_{53}N_6O_4$ 753.4128; Found 753.4128.

Synthesis of reference propargyl derivative (3e).

A suspension of **3d** (1.20 g, 5.08 mmol) and K_2CO_3 (2.80 g, 20.32 mmol) was heated at reflux for 1 h in dry acetone (70 mL), and a solution of propargyl bromide (1.20 g, 10.16 mmol) in dry acetone (10 mL) was added. The reaction mixture was refluxed for 17 h. The solvents were evaporated and the residue partitioned between 10% HCl and CH_2Cl_2. The organic layer was separated and dried ($MgSO_4$) and the solvents were evaporated. The residue eluted from a column chromatography column of silica gel with CH_2Cl_2/Hexane (1:1) gave the desired product **3e** (1.30 g, 94%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.28 (9H, s, t*Bu*), 2.29 (s, 6H, CH_3) 2.51 (d, *J* = 2.3 Hz, 1H, *HC*C), 4.45 (s, 2H, HCCCH_2O–), 4.82 (d, *J* = 2.2 Hz, 4H, –OCH_2COO–) and 7.00 (s, 2H, Ar*H*) ppm. ^{13}C NMR (100 MHz) δ 16.6, 31.5, 34.1, 52.4, 69.0, 75.5, 77.1, 125.9, 129.7, 147.1, 153.0 and 168.5 ppm. HRMS (ESI/TOF-Q) *m/z*: $[M]^+$ Calcd for $C_{17}H_{22}O_3$ 274.1569; Found 274.1600.

A similar procedure using **3a** was followed for the synthesis of **3b**.

Reference propargyl derivative (3b) was obtained as a colorless oil (1.15 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.28 (s, 9H, t*Bu*), 2.31 (s, 6H, CH_3) 2.49 (s, 1H, *HC*C), 4.47 (s, 2H, HCCCH_2O–) and 7.00 (s, 2H, Ar*H*) ppm. ^{13}C NMR (100 MHz) δ 16.7, 16.8, 31.4, 31.5, 34.1, 59.72, 59.76, 59.80, 74.6, 74.8, 79.58, 79.62, 125.7, 130.2, 146.9 and 153.0 ppm. HRMS (ESI/TOF-Q) *m/z*: $[M]^+$ Calcd for $C_{15}H_{20}O$ 216.1514; Found 216.1451.

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charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 144 1223 336033 or e-mail: depost@ccdc.cam.ac.uk].

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