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Reaction Mechanisms

A Rare and Exclusive Endoperoxide Photoproduct Derived from a Thiacalix[4]arene Crown-Shaped Derivative Bearing a 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 $\lambda = 365$ nm; the structure was unambiguously confirmed by $^{1}H/^{13}C$ NMR spectroscopy and X-ray crystallography. The prerequisites for the formation of the endoperoxide photoproduct have also been discussed. Furthermore, the photochemical reaction rate could be greatly enhanced in the presence of the thiacalix[4]arene platform because it served as a host to capture oxygen.

Introduction

Photochemical reactions have found widespread utility in biological and polymer science given that the use of photons as a "reagent" is considered the least invasive switching stimulus, that is, not requiring addition of any external chemical species.[1] Of the many photochemical reaction systems known, anthracene and its derivatives are of special interest owing 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 nonselective, 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] whereas 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; these products tend to be overlooked by scientists owing to their negligible yield.[6,8] Indeed, reports related to the direct characterization of the photoproducts only describe UV/Vis 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 because of the unlimited possibilities for functionalization on the lower-rim, upper-rim, and bridging sulfur atoms with various conformations.[9a] Herein, we report the synthesis and characterization of a series of novel thiacalix[4]arene derivatives (**T1**, **T2**, and **T3**), which contain the anthracene moiety. Among them, derivative **T1**, with the 9,10-substituted anthracene group, is of special interest. The photochemical behavior of **T1** in solution is described and 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 copper(I)-catalyzed 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 hydrogen atoms of **1 d**[10] disappeared, whereas a new singlet at $\delta = 7.40$ ppm was attributed to the protons of the newly formed triazole skeleton. Two singlets for the *tert*-butyl protons were found unusually upfield, namely, at $\delta = 0.79$ and 0.30 ppm (owing to the additional shielding effect of the anthracene moiety); there are two singlets for the aromatic protons at $\delta = 7.09$ and 7.29 ppm. All of these signals are indicative of the C_2-symmetric structure of **T1** in the 1,3-alternate conformation (Figure S1 in the Supporting Information).

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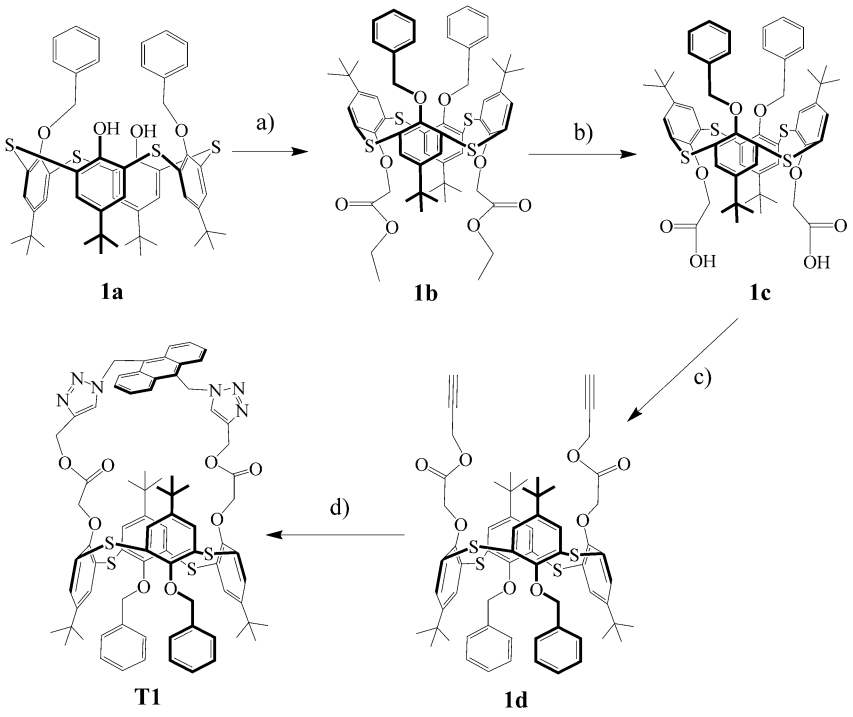
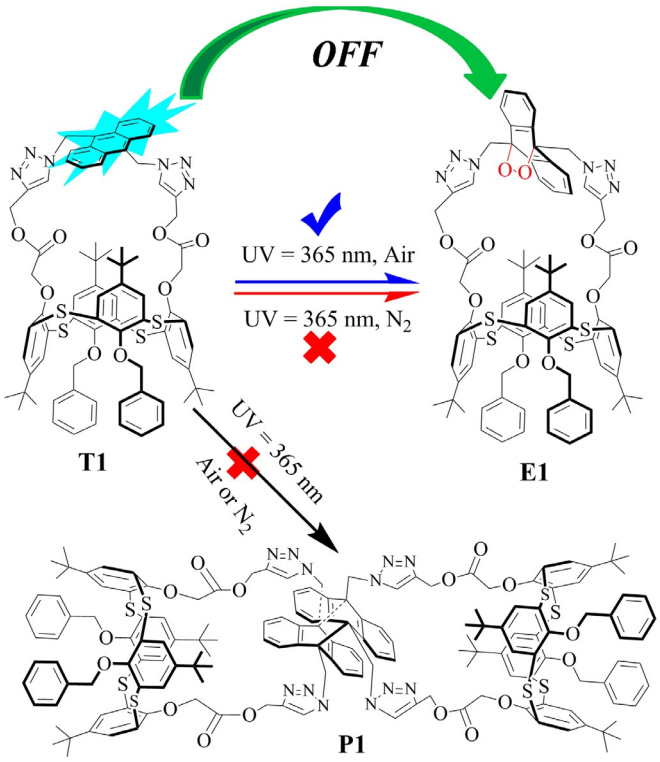


Scheme 1. The synthetic route to thiacalix[4]arene crown-shaped derivative **T1**: a) Cs_2CO_3, 2-bromoethyl acetate, acetone, reflux; b) NaOH, tetrahydrofuran (THF)/H_2O = 1:1, reflux; c) K_2CO_3, propargyl bromide, acetone, reflux; d) CuI, 9,10-bis(azidomethyl)anthracene, THF/H_2O = 4:1, reflux.

The target thiacalix[4]arene derivative **T1**, which possesses a crown-shaped thiacalix[4]arene recognition motif functionalized with the anthracene moiety at the 9,10-positions, was employed as the photoactive unit. The use of **T1** had the advantage of limiting the possible photoproduct regioisomers to 1) an intermolecular photodimerization isomer (**P1**) and 2) an intramolecular endoperoxide isomer (**E1**; 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 $\lambda = 365$ nm under air. Upon irradiation, a new group of proton signals (red in Figure 1) immediately appeared with a concomitant decrease in the concentration of **T1** (blue in Figure 1). An indication of the photochemical reaction process was the signals of the anthracene proton resonances ($\delta = 7.83$ and 8.65 ppm), which gradually decreased and finally disappeared. Upon gradually increasing the irradiation time, the conversion yield gradually increased, as expected. After 90 min, quantitative conversion was indicated by the complete disappearance of all **T1** proton resonances, and a new unambiguous group of signals appeared. The photoactive anthracene motif resulted in xylene-like units, for which proton signals appeared at $\delta = 7.35$ and 7.58 ppm (for characterization data, see Figure S4 in the Supporting Information). The unusually upfield *tert*-butyl protons ($\delta = 0.30$ ppm) dramatically shifted back to their "normal" chemical shift position ($\delta = 0.89$ ppm) owing 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 signal of the photoproduct at $\delta =$ 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 in the Supporting Information). The resulting UV ab-



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

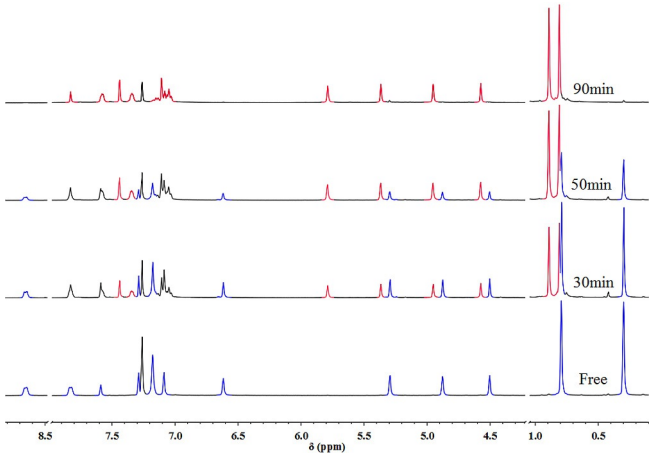


Figure 1. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) spectra of a 6 mM solution of **T1** after irradiation at $\lambda = 365$ nm (0, 30, 50, 90 min).

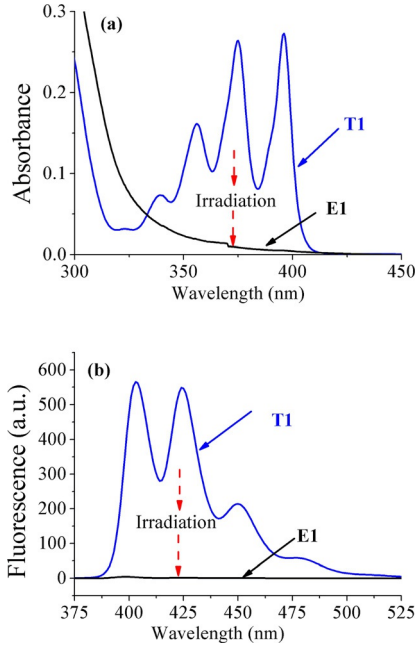


Figure 2. UV/Vis (a) and fluorescence (b) spectra of a 2.4×10^{-5} M solution of **T1** in $CHCl_3$ under irradiation.

sorption spectrum of **T1** after irradiation (Figure 2a) fully supported the formation of planar-symmetric photoproducts that involved only the central anthracene ring and not the lateral anthracene aromatic rings, that is, there was no absorption beyond $\lambda = 300$ nm.[4a] A similar conclusion can be drawn from fluorescence studies (Figure 2b). The characteristic anthracene moiety emission of **T1** in the $\lambda = 375$–525 nm region was switched "off" after irradiation, which mirrored the formation of the non-fluorescence photoproduct. In contrast, a 6 mM solution of **T1** in degassed $CDCl_3$ was irradiated at $\lambda = 365$ nm under a nitrogen atmosphere. No detectable changes were observed in the ^{1}H 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 because of the numerous photoproducts possible. Even for our simplest system, there are two possible photoproduct isomers: **E1** and **P1**. Fortunately, quantitative conversion provided a pure photoproduct, which was easily confirmed by mass spectrometry. The observed signals at *m/z* 1413.4907 $[M+H]^+$ (Figure S6 in the Supporting Information) and 1380.4910 $[M]^+$ for unirradiated **T1** (Figure S3 in the Supporting Information) 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. $C_{80}H_{80}N_6O_{10}S_4{\cdot}2(CH_4O)$,

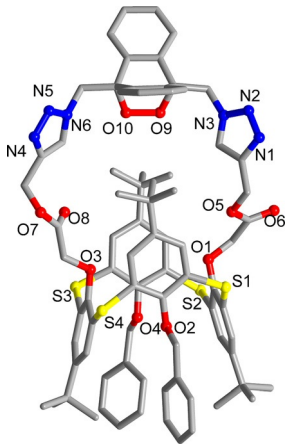
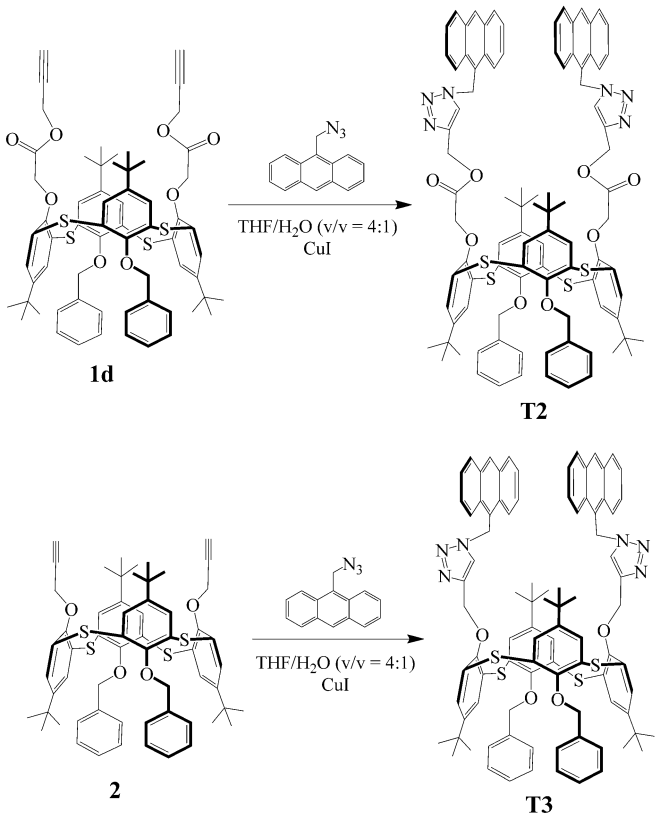


Figure 3. Single-crystal structure of **E1**. Hydrogen atoms and two methanol molecules of crystallization have been omitted for clarity.

one endoperoxide photoproduct **E1** in 1,3-alternate conformation, and two molecules of methanol were in the asymmetric unit (Figure S7 in the Supporting Information). 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 expected [4+4] photodimerization reaction had not occurred, but rather an unexpected [4+2] photosensitized oxygenation occurred involving the cycloaddition of $^1O_2$ (singlet oxygen, an excited state of molecular oxygen generated from ambient air by direct irradiation with UV light)[8] with the electron-rich carbon atoms of the central anthracene ring.[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; this may be attributed to the inwardly crown-shaped structure required to trap singlet oxygen.[9b]

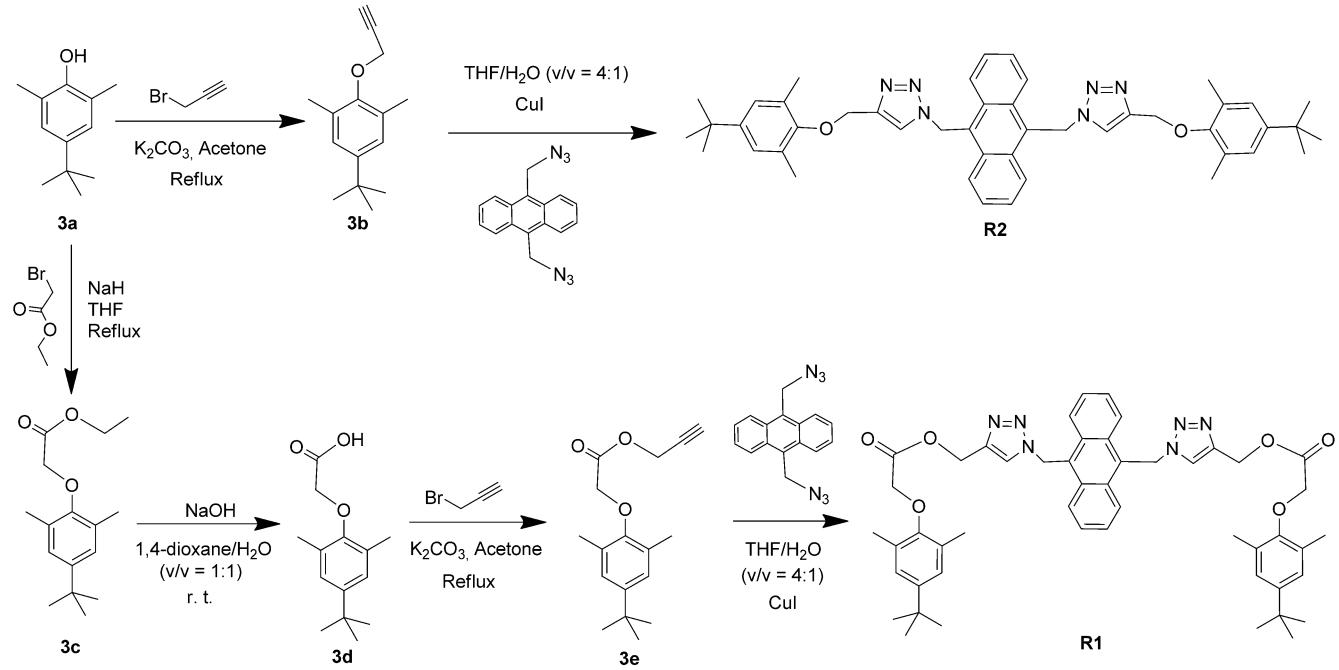
To further investigate the rare endoperoxide photochemical phenomenon, compounds **T2**, with a 9-substituted anthracene moiety as the photoactive unit, and **T3**, with a similar structure but short linkage, have been introduced (Scheme 3). Interestingly, the UV absorption and fluorescence spectra of compounds **T2** and **T3**, which were quenched after irradiation, were almost the same as those of compound **T1** (Figure S8 in the Supporting Information). Unfortunately, the ^{1}H NMR spec-



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

tra gradually changed to become very complicated, and could not be used to identify any of the photoproducts when compounds **T2** or **T3** were irradiated under the same conditions as those used for compound **T1** (Figures S9 and S10 in the Supporting Information). The observed phenomena in **T2** and **T3** were similar to most reported results crudely defined as photodimerization.[2–8] It strongly suggested that the 9,10-substituted anthracene crown-shaped moiety of compound **T1** was the key factor for the formation of this rare endoperoxide photoproduct.

Furthermore, two reference compounds, **R1** and **R2**, possessing 9,10-substituted anthracene with different linkages were also synthesized (Scheme 4). The photochemical reaction processes of **R1** and **R2** were also investigated by ^{1}H NMR and UV absorption spectroscopy. Surprisingly, all of the results were similar to those of thiacalix[4]arene derivative **T1**. The UV absorption spectra of **R1** and **R2** were quenched after irradiation (Figure S11 in the Supporting Information); a quantitative conversion was observed, such that all proton resonances of **R1** or **R2** were replaced by a new unambiguous group of signals after irradiation (Figures S12 and S13 in the Supporting Information). All of the observed results strongly suggested that endoperoxide photoproducts were also formed during these photochemical processes of **R1** and **R2**. In other words, the compounds that possessed 9,10-substituted anthracene in a symmetric structure (RCH_2—anthracene—CH_2R) were favorable in the formation of the endoperoxide photoproduct, rather than the dimerization photoproduct. However, more interestingly, we should point out that the time it took to complete the photochemical reactions of **T1**, **R1**, and **R2**, to form the corresponding products **E1**, **E2**, and **E3**, was 90, 140, and 120 min, respectively (Figure 4). The thiacalix[4]arene platform may serve as a host to capture oxygen, which is conducive to the formation of the endoperoxide photoproduct. This hypothesis was consistent with the unique X-ray diffraction results for the position of the —O10—O9— bond, which was oriented



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

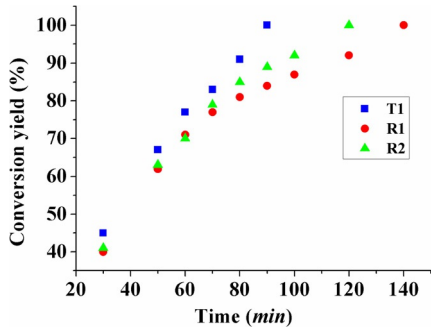


Figure 4. Conversion yield versus reaction time of 6 mM solutions of **T1**, **R1**, and **R2** in $CDCl_3$ under irradiation at $\lambda = 365$ nm.

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 revealed that the decomposition of photoproducts occurs either thermally (≈60 °C) or by irradiation with deep UV light ($\lambda < 300$ nm), or can even occur naturally.[2b,11] However, in our case, the thermal cycloreversion of 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 a solution of **E1** at $\lambda = 254$ 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 suggest that the **E1** photoproduct is very stable under these conditions.

Singlet oxygen ($^1O_2$) is an excited state of molecular oxygen that has attracted great interest because $^1O_2$ 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 owing to its short lifetime.[12] Monitoring the direct emission of $^1O_2$ at $\lambda = 1270$ nm is the most common method,[13c] but such detection is limited by low sensitivity.[15e] To improve the sensitivity, fluorimetry is the first choice and can be rapidly performed, is nondestructive, and has greater sensitivity.[7a,16] Indeed, scientists have successfully designed fluorescent probes that trap $^1O_2$ to give a sensitive fluorescence response.[16] However, designing a suitable $^1O_2$ fluorescent probe is still a big challenge. Modified **T1**, with an anthracene functionality, allows for a rapid reaction with low concentrations of $^1O_2$ concomitant with UV/Vis and fluorescence spectral changes at room temperature. In other words, compound **T1** has potential applications as a high selectivity and high sensitivity chemosensor for the detection of singlet oxygen. Current studies are aimed to explore **T1** as a practical chemosensor for singlet oxygen.

Conclusion

The synthesis of a new thiacalix[4]arene crown-shaped derivative **T1** was reported, and the photochemical behavior was investigated by ^{1}H NMR, UV/Vis, and fluorescence spectroscopy. We have demonstrated that the photochemical reaction of **T1** (containing anthracene moieties) converted it into the endoperoxide **E1** in quantitative yield upon irradiation at $\lambda = 365$ 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 compounds possessing 9,10-substituted anthracene in a symmetric structure (RCH_2–anthracene–CH_2R) were favorable to form the endoperoxide photoproduct rather than the dimerization photoproduct. Furthermore, the photochemical reaction rate could be greatly enhanced in the presence of a thiacalix[4]arene platform; this was attributed to the thiacalix[4]arene platform serving as a host to capture oxygen.

Experimental Section

General Procedures

All melting points (Yanagimoto MP-S1) are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian-400MR-vnmrs400 spectrometer 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 by using a direct-inlet system. UV/Vis spectra were recorded by using a Shimadzu UV-3150UV/Vis/near-IR 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 $\lambda = 365$ nm was performed with a UV lamp (AH 400PR, AC 100 V, 60 Hz). Irradiation at $\lambda = 254$ nm was performed with a 4 W 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. Compounds **1a**,[17] **1b**,[18] **1c**,[18] **1d**,[10] **2**,[19] **3a**,[20] **3c**,[21] **3d**,[21] 9-(azidomethyl)anthracene,[22] and 9,10-bis(azidomethyl)anthracene[23] were prepared by following reported procedures. All solvents used were dried and distilled by standard 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 THF/H_2O (75 mL, 4:1) and heated at reflux for 15 h. The resulting solution was cooled and diluted with water and extracted with CH_2Cl_2. The organic layer was separated, dried ($MgSO_4$), and evaporated to give the solid crude product. The residue was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (20:1) and gave the desired product **T1** (100 mg, 36%) as a light yellow powder. M.p. 361–362 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.30$ (s, 18H; *tBu*), 0.79 (s, 18H; *tBu*), 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*),

8.65–8.66 ppm (m, 4H; An-*H*); ^{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, 168.3 ppm; HRMS (FAB): *m/z* calcd for $C_{80}H_{80}N_6O_8S_4$ $[M]^+$: 1380.4921; found: 1380.4910.

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

Thiacalix[4]arene Derivative T2

Thiacalix[4]arene derivative **T2** was obtained as a light yellow solid (column chromatography on 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; *tBu*), 1.01 (s, 18H; *tBu*), 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; -TriazoleCH$_2$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*), 8.57 ppm (s, 2H; An-*H*); ^{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, 167.6 ppm; HRMS (FAB): *m/z* calcd for $C_{94}H_{91}N_6O_8S_4$ $[M+H]^+$: 1559.5781; found: 1559.5780.

Thiacalix[4]arene Derivative T3

Thiacalix[4]arene derivative **T3** was obtained as a light yellow solid (column chromatography on 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; *tBu*), 1.20 (s, 18H; *tBu*), 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*), 8.51 ppm (s, 2H; An-*H*); ^{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, 157.5 ppm; HRMS (FAB): *m/z* calcd for $C_{90}H_{87}N_6O_4S_4$ $[M+H]^+$: 1443.5672; found: 1443.5670.

Reference Compound R1

Reference compound **R1** was obtained as a light yellow solid (column chromatography on 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; *tBu*), 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; -TriazoleCH$_2$An), 6.94 (s, 4H; Ar*H*), 7.32 (s, 2H; Triazole-*H*), 7.67–7.70 (m, 4H; An-*H*), 8.43–8.46 ppm (m, 4H; An-*H*); ^{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, 169.1 ppm; HRMS (FAB): *m/z* calcd for $C_{50}H_{57}N_6O_6$ $[M+H]^+$: 837.4340; found: 837.4376.

Reference Compound R2

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; *tBu*), 2.13 (s, 12H; *CH*$_3$), 4.80 (s, 4H;-O*CH*$_2$Triazole-), 6.63 (s, 4H; -TriazoleCH$_2$An), 6.91 (s, 4H; Ar*H*), 7.30 (s, 2H; Triazole-*H*), 7.68–7.71 (m, 4H; An-*H*), 8.48–8.50 ppm (m, 4H; An-*H*); ^{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, 152.9 ppm; HRMS (FAB): *m/z* calcd for $C_{46}H_{53}N_6O_2$ $[M+H]^+$: 721.4230; found: 721.4244.

Photoproduct from T1 (E1)

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; *tBu*), 0.89 (s, 18H; *tBu*), 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, 8H; 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*), 7.83 ppm (s, 2H; Triazole-*H*); ^{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, 168.5 ppm; HRMS (FAB): *m/z* calcd for $C_{80}H_{81}N_6O_{10}S_4$ $[M+H]^+$: 1413.4897; found: 1413.4907.

Photoproduct from R1 (E2)

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; *tBu*), 2.22 (s, 12H; *CH*$_3$), 4.39 (s, 4H; -O*CH*$_2$COO), 5.31 (s, 4H; -O*CH*$_2$Triazole-), 5.75 (s, 4H; -TriazoleCH$_2$C), 6.96 (s, 4H; Ar*H*), 7.26 (s, 4H; Ph-*H*), 7.43 (s, 4H; Ph-*H*), 8.00 ppm (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, 169.0 ppm; FABMS: *m/z* calcd for $C_{50}H_{57}N_6O_8$ $[M+H]^+$: 869.4238; found: 869.4236.

Photoproduct from R2 (E3)

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; *tBu*), 2.25 (s, 12H; *CH*$_3$), 4.92 (s, 4H; -O*CH*$_2$Triazole-), 5.78 (s, 4H; -TriazoleCH$_2$C), 6.99 (s, 4H; Ar*H*), 7.26–7.27 (m, 4H; Ph-*H*), 7.46–7.48 (m, 4H; Ph-*H*), 8.00 ppm (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, 153.2 ppm; HRMS (FAB): *m/z* calcd for $C_{46}H_{53}N_6O_4$ $[M+H]^+$: 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 heated at reflux for 17 h. The solvents were evaporated and the residue was partitioned between 10% HCl and CH_2Cl_2. The organic layer was separated, dried ($MgSO_4$), and the solvents were evaporated. The residue was eluted from a column of silica gel with CH_2Cl_2/Hexane (1:1) to give the desired product **3e** (1.30 g, 94%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 9H; *tBu*), 2.29 (s, 6H; *CH*$_3$) 2.51 (d, *J* = 2.3 Hz, 1H; *HCC*), 4.45 (s, 2H; HCC*CH*$_2$O-), 4.82 (d, *J* = 2.2 Hz, 4H; -O*CH*$_2$COO-), 7.00 ppm (s, 2H; Ar*H*); ^{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, 168.5 ppm; HRMS (ESI/TOF-Q): *m/z* calcd for $C_{17}H_{22}O_3$ $[M]^+$: 274.1569; found: 274.1600.

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

Reference Propargyl Derivative 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; *tBu*), 2.31

(s, 6H; CH_3) 2.49 (s, 1H; HCC), 4.47 (s, 2H; HCCCH_2O-), 7.00 ppm (s, 2H; ArH); ^{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, 153.0 ppm; HRMS (ESI/TOF-Q): *m/z* calcd for $C_{15}H_{20}O$ $[M]^+$: 216.1514; found: 216.1451.

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