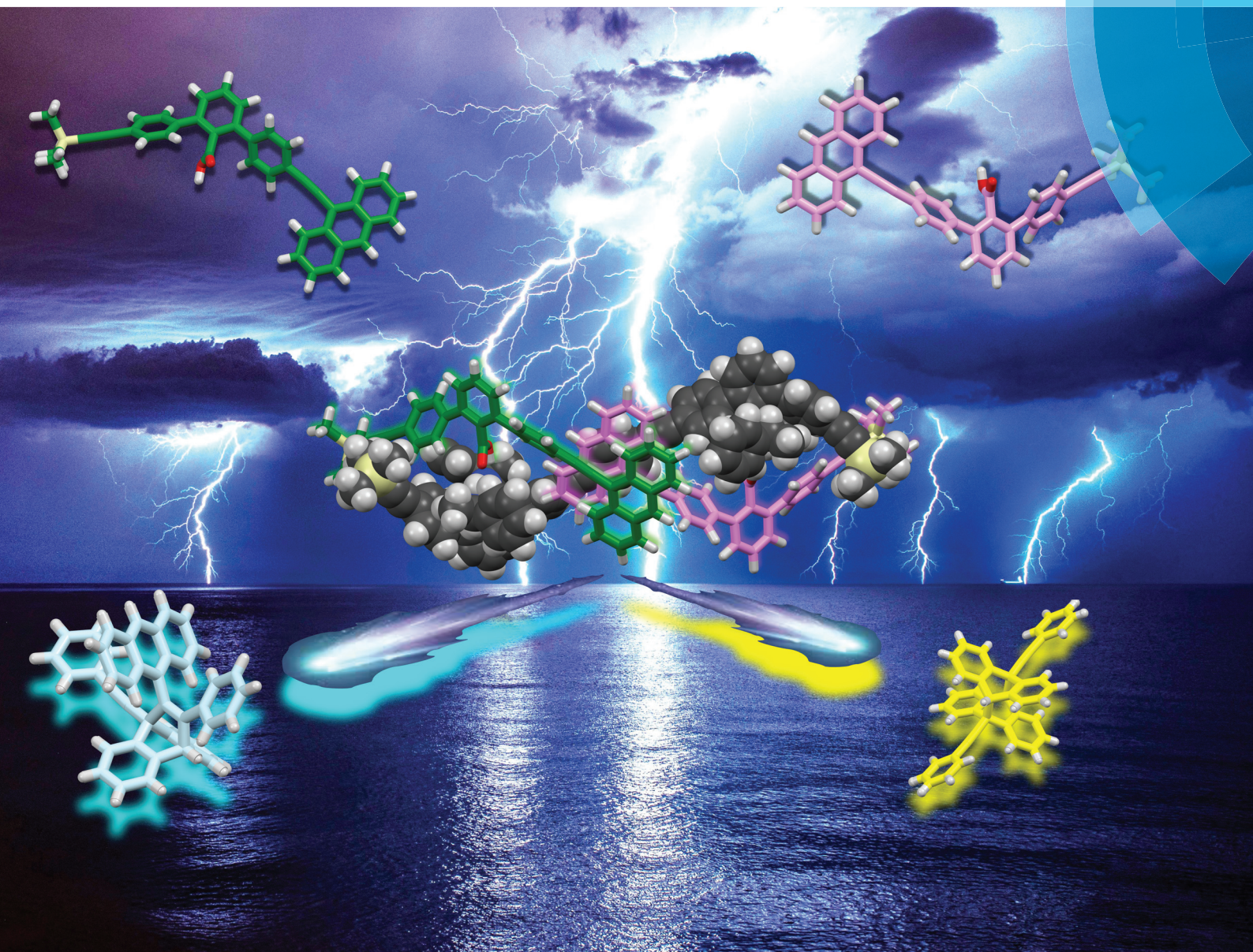


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PAPER

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Remarkable acceleration of template-directed photodimerisation of 9-phenylethynylantracene derivatives assisted by complementary salt bridge formation

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Remarkable acceleration of template-directed photodimerisation of 9-phenylethynylantracene derivatives assisted by complementary salt bridge formation†

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The photoirradiation of 9-phenylethynylantracene in degassed chloroform and benzene afforded not only a [4 + 2]-*anti* Diels–Alder addition dimer, but also a [4 + 4]-*anti*-dimer as a minor product for the first time as revealed by single-crystal X-ray analysis, while the anthracene residue was quantitatively oxidised in undegassed dilute chloroform, giving the corresponding endoperoxides. The photochemical reactions of carboxylic acid monomers bearing a 9-phenylethynylantracene unit at one and both ends were further investigated in the presence and absence of the complementary amidine dimer as the template. It was found that a similar photooxidation reaction of the monomers was significantly suppressed in the presence of the template even in undegassed chloroform. In addition, the template-directed photodimerisation of the mono- and di-9-phenylethynylantracene-bound monomers was remarkably accelerated 30- or 61-fold in the degassed chloroform, giving the [4 + 2]-*anti*- and [4 + 4]-*anti*-dimers as major and minor products, respectively, whereas the di-9-phenylethynylantracene-bound monomer was preferentially photo-polymerised in the absence of the template.

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Introduction

Photochemical reactions often promote the formation of products inaccessible by thermal reactions, leading to one of the key reactions in the state-of-the-art organic synthesis.¹ However, it remains difficult to control the selectivity and specificity during the photochemical transformations in homogeneous solutions in a predictable way, thus producing a mixture of regioisomers along with stereoisomers. Therefore, the template-directed photoreaction has been developed not only to improve the efficiency, but also to control the regioselectivity and/or enantioselectivity.²

Among a variety of photoreactions, the photodimerisation of anthracene and its derivatives is one of the most well-known photochemical reactions and has been extensively investigated.³ The photodimers are connected by two covalent bonds resulting from the [4 + 4] cycloaddition and revert to anthracenes thermally or under UV irradiation by using light below 300 nm. Taking advantage of this feature, the anthracene skel-

eton has been successfully applied to two-dimensional polymers,⁴ supramolecular polymers,⁵ reversible cross-linking reactions,⁶ photochemical molecular switches⁷ and photoinduced shape-changeable materials.⁸ Another important synthetic feature during the anthracene photodimerisation is that substituted anthracenes at specific positions afford regio- and/or stereoisomers.³ For instance, the irradiation of 9-substituted anthracenes gives two regioisomeric dimers, the [4 + 4]-*anti* and -*syn* photodimers (Fig. 1a), and the thermodynamically stable [4 + 4]-*anti* dimer is, in general, produced as a major product, whereas the energetically unfavourable [4 + 4]-*syn* dimer is regioselectively formed in specific environments, such as within micelles.⁹ Supramolecular approaches using cyclic host molecules with a rigid concave cavity, such as cyclodextrins^{5f,10} and cucurbit[*n*]urils,^{5d,e,6e,10f,h} capable of encapsulating two anthracene molecules in close proximity, and DNA as a template,¹¹ have also been developed to improve the reaction yield and to control the regio- and stereo-selectivities during the photodimerisation of anthracene and its derivatives.

On the other hand, when exposed to light in the presence of oxygen, anthracene derivatives readily react with singlet oxygen to produce endoperoxides,¹² which eventually revert to the parent anthracenes and oxygen under thermolysis (Fig. 1a). However, anthracene can be effectively protected from photooxidation and dimerised in the cavity of cyclo-

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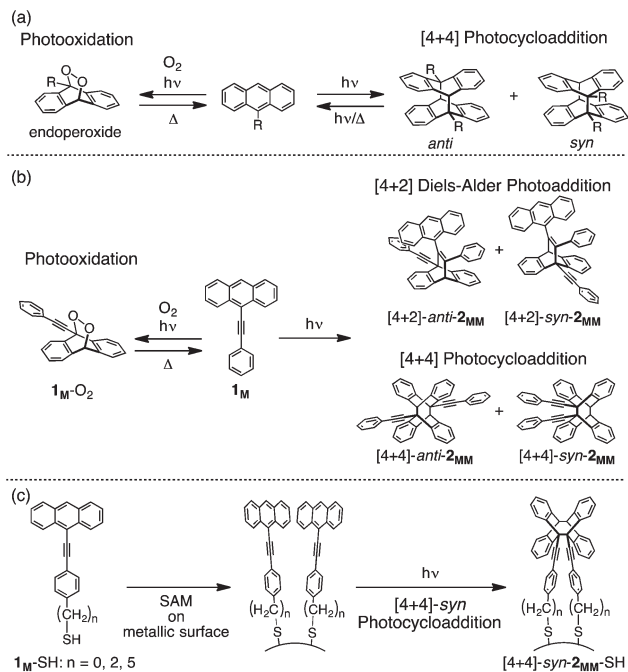


Fig. 1 Photoreaction of (a) 9-substituted anthracene, (b) 9-phenylethynylanthracene ($\mathbf{1}_M$) and (c) 9-(4-mercaptoalkylphenylethynyl)anthracenes ($\mathbf{1}_M$ -SH) and their photoproducts.

dextrin^{5f,10} and in the crystal state^{12e} even in the presence of oxygen.

Becker and Andersson reported that the irradiation of 9-phenylethynylanthracene ($\mathbf{1}_M$) in solution readily promoted a [4 + 2] Diels–Alder addition reaction between the ethynyl moiety and the central ring of the other anthracene residue of $\mathbf{1}_M$ over the [4 + 4] cycloaddition reaction, predominantly producing a [4 + 2]-*anti* dimer ([4 + 2]-*anti*- $\mathbf{2}_{MM}$, Fig. 1b).¹³ In contrast, Weiss and co-workers demonstrated the energetically unfavourable [4 + 4]-*syn* dimer formation of thiolated 9-phenylethynylanthracenes ($\mathbf{1}_M$ -SH) (Fig. 1c) upon irradiation that proceeded in a highly regioselective manner when $\mathbf{1}_M$ -SH was mixed in self-assembled alkane thiolate monolayers on flat Au surfaces on which the anthracene moieties were favourably arranged in such a way that the intermolecular [4 + 4]-*syn* cycloaddition ([4 + 4]-*syn*- $\mathbf{2}_{MM}$) could be possible.¹⁴ The regioselective [4 + 4]-*syn* dimer formation was monitored by scanning tunneling microscopy (STM)^{14a} and surface-enhanced Raman spectroscopy (SERS),^{14b} thus showing a significant decrease in conductivity and disappearance of the peaks due to the anthracene moiety, respectively. Recently, Klajn and co-workers also demonstrated that $\mathbf{1}_M$ -SH immobilised on metallic (Au and Pd) nanoparticles dimerised in a regioselective way to yield a [4 + 4]-*syn* cycloaddition product under photoirradiation (Fig. 1c), based on the time-dependent absorption spectral changes.¹⁵

We previously reported a series of *m*-terphenyl-based complementary double helices that could be rationally designed and synthesised based on a modular strategy we developed using

amidinium–carboxylate salt bridges through which the double helices are stabilised by double hydrogen bonds with a well-defined directionality even in polar solvents.¹⁶ Therefore, various types of functional linkers, such as Pt(η)-acetylide^{16b,e,j,l,n} and azobenzene linkages,^{16d,l,m} can be introduced between the *m*-terphenyl units while maintaining the double-helical structures.¹⁶ The complementary double-helical framework stabilised by salt bridges has recently been applied to the template-directed synthesis of complementary double helices through imine-bond forming reactions between a carboxylic acid and amidine monomers bearing either a formyl or an amino group at one end.^{16i,m} The complementary dimeric templates linked by an azobenzene residue significantly accelerated the imine-bond forming reactions. However, the reactions along the complementary dimer strands as a template were limited to imine-bond forming reactions.

In this work, we synthesised new carboxylic acid monomers ($\mathbf{1}_C$ and $\mathbf{3}_C$) bearing an anthracene group at one and both ends (Fig. 2a), respectively, and investigated their template-directed photodimerisation reactions in solution in the absence and presence of the complementary amidine dimer (\mathbf{T}_{AA}) connected by a *p*-diethynylbenzene unit as the template (Fig. 2d). The monomers $\mathbf{1}_C$ and $\mathbf{3}_C$ possess one or two 9-phenylethynylanthracene moieties identical to $\mathbf{1}_M$, hence we anticipated the regioselective photodimerisation or polymerisation of $\mathbf{1}_C$ or $\mathbf{3}_C$, respectively, giving products with a specific regioselectivity among the following four possible regioisomers ([4 + 2]-*anti*-, [4 + 2]-*syn*-, [4 + 4]-*anti*- and [4 + 4]-*syn*-isomers, Fig. 2b and c) along with acceleration of the photoreactions in the presence of the rigid template \mathbf{T}_{AA} through the salt bridges, which permit the 9-phenylethynylanthracene moieties to be arranged in close proximity (Fig. 2d).

For comparison, the photochemical dimerisation of $\mathbf{1}_M$ (Fig. 1b),¹³ a model compound of $\mathbf{1}_C$ and $\mathbf{3}_C$, was also thoroughly investigated under various conditions. We found that a [4 + 4]-*anti*-dimer ([4 + 4]-*anti*- $\mathbf{2}_{MM}$) was also produced as a minor product along with the major Diels–Alder addition product, [4 + 2]-*anti*- $\mathbf{2}_{MM}$, (Fig. 1b) and then their structures were unambiguously determined by single-crystal X-ray analysis.

Results and discussion

Synthesis

9-Phenylethynylanthracene ($\mathbf{1}_M$) was prepared according to the reported method.¹⁷ The achiral carboxylic acid monomers ($\mathbf{1}_C$ and $\mathbf{3}_C$) bearing an anthracene group at one and both ends were newly synthesised according to Schemes S3 and S5,† respectively, (see the ESI†). The *p*-phenylene-linked optically active amidine dimer (\mathbf{T}_{AA})^{16g} and its monomeric amidine (\mathbf{A})^{16a} were also prepared according to the reported methods.

Photoreactions of model monomer ($\mathbf{1}_M$)

The photoreaction of $\mathbf{1}_M$ (0.50 mM) was first investigated in undegassed CDCl_3 at 25 °C (run 1 in Table 1) upon light



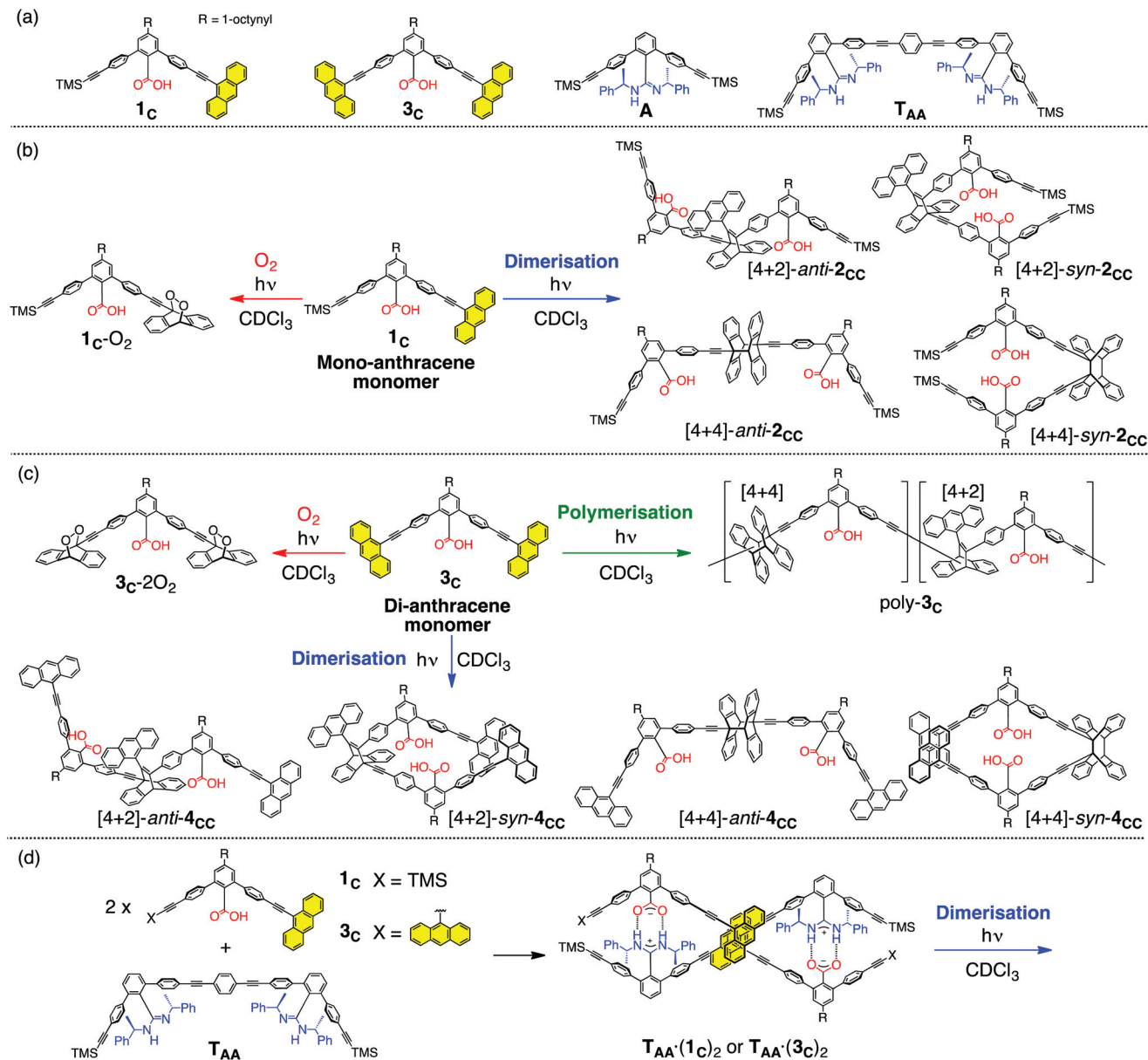


Fig. 2 (a) Chemical structures of 9-phenylethynylantracene-bound carboxylic acid monomers ($1c$ and $3c$), monomeric amidine (A) and dimeric amidine template (T_{AA}). (b and c) Possible photoreactions (photooxidation and cycloaddition reactions) of the carboxylic acid monomers (b) $1c$ and (c) $3c$ and their photoproducts. (d) Schematic illustration for the template-directed photodimerisation of the 9-phenylethynylantracene-bound monomers ($1c$ and $3c$).

irradiation over 400 nm. Reaction progress was monitored by 1H NMR spectroscopy. The peak intensity of the anthracene proton (H_a) at the 10-position in 1_M decreased with time, whereas a new singlet signal appeared in a relatively low magnetic field of 6.08 ppm, which can be assigned to the bridge-head proton (H_b) of endoperoxide (1_M-O_2) and its peak intensity gradually increased as the reaction progressed, reaching 89% after irradiation for 3 min (Fig. 3a and S6a†). This assignment was supported by a molecular ionic peak at $m/z = 309.19$ ($[1_M-O_2-H]^-$) in its negative-mode electron-spray ionisation (ESI) mass spectrum of the reaction mixture and also by the absorption spectrum of 1_M after irradiation for 3 min, in

which the peaks due to the anthracene moiety almost disappeared (Fig. S6†). It was noted that the obtained 1_M-O_2 was not stable in solution and was thermally converted back to 1_M without decomposition at 25 °C.^{12b,df} Thus, the rate constant for the retro-photooxidation reaction was estimated to be $4.7 \times 10^{-6} s^{-1}$ on the basis of the time-dependent 1H NMR spectral changes (Fig. S7†).

In contrast, after light irradiation of 1_M (0.50 mM) for 30 min in degassed $CDCl_3$ at 25 °C (run 5 in Table 1), the 1H NMR spectrum showed two new sets of singlet peaks due to the bridge-head protons (H'_b and H''_b) along with a new anthracene proton (H'_a), indicating the formation of two



Table 1 Results of photoreactions of **1_M** under various reaction conditions

Run	1_M Solvent (conc. (mM))	Irradiation time (min)	Conv. (%) (consumption rate $10^{-3} k$ (s ⁻¹))	Product yield (%) (Reaction rate $10^{-3} k$ (s ⁻¹))				Sup. Fig. no.
				1_M -O ₂	[4 + 2]- <i>anti</i> -2 _{MM}	[4 + 4]- <i>anti</i> -2 _{MM}	[4 + 2]/ [4 + 4]	
1	Undegassed CDCl ₃ (0.50)	3	89 (16)	89 (16)	—	—	—	Fig. S6
2	Undegassed CDCl ₃ (8.0)	30	88 (2.0)	12 ^a (0.71)	60 (0.93)	14 (0.14)	4.3	Fig. S8
3	Undegassed benzene- <i>d</i> ₆ (0.50)	16	88 (3.2)	32 ^b (1.0)	42 (0.96)	8 (0.14)	5.3	Fig. S9
4	Undegassed benzene- <i>d</i> ₆ (8.0)	30	96 (1.9)	9 ^c (0.37)	70 (1.0)	12 (0.13)	5.8	Fig. S10
5	Degassed CDCl ₃ (0.50)	30	88 (1.7)	—	64 (1.1)	23 (0.21)	2.8	Fig. S11
6	Degassed CDCl ₃ (8.0)	45	95 (1.5)	—	77 (1.0)	18 (0.15)	4.3	Fig. S12
7	Degassed benzene- <i>d</i> ₆ (0.50)	30	90 (1.6)	—	74 (1.1)	15 (0.16)	4.9	Fig. S13
8	Degassed benzene- <i>d</i> ₆ (8.0)	45	97 (1.3)	—	80 (1.0)	15 (0.13)	5.3	Fig. S14
9	Degassed benzene (8.0)	90	— ^d	— ^d	75	8	9.4	Ref. 13

^a The maximum yield of **1_M**-O₂ was 18% after 8 min irradiation of light (>400 nm) (see Fig. S8a). ^b The maximum yield of **1_M**-O₂ was 38% after 8 min irradiation of light (>400 nm) (see Fig. S9a). ^c The maximum yield of **1_M**-O₂ was 15% after 8 min irradiation of light (>400 nm) (see Fig. S10a). ^d Not available in ref. 13.

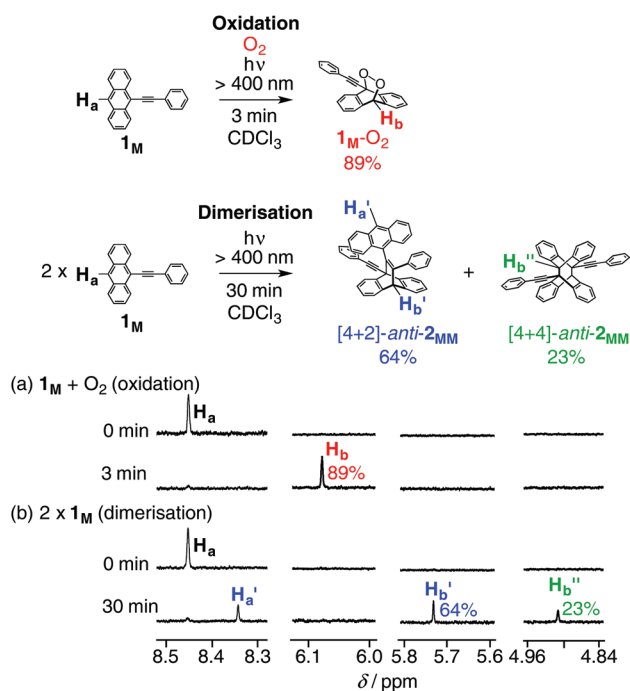


Fig. 3 Partial ¹H NMR (500 MHz, 25 °C) spectra of **1_M** (0.50 mM) in (a) (run 1 in Table 1) undegassed and (b) (run 5 in Table 1) degassed CDCl₃ before (top) and after (bottom) irradiation of light (>400 nm). Full-scale spectra are shown in Fig. S6a and S11a,† respectively.

photodimers (Fig. 3b and S11a†), which were unambiguously identified as [4 + 2]-*anti*-2_{MM} and [4 + 4]-*anti*-2_{MM}, respectively, by X-ray crystallographic analyses (Fig. 4) together with 2D NMR spectroscopy (Fig. S41 and S44†). Becker and Andersson reported that the photoreaction of **1_M** (8.0 mM) in degassed benzene gave [4 + 2]-*anti*-2_{MM} in *ca.* 75% yield together with a by-product (*ca.* 8%) which was assumed to be an intermolecular [4 + 4] cycloadduct in spite of no structural information (run 9 in Table 1).¹³ Thus, we examined the photoreaction of **1_M** (8.0 mM) under almost the same conditions in

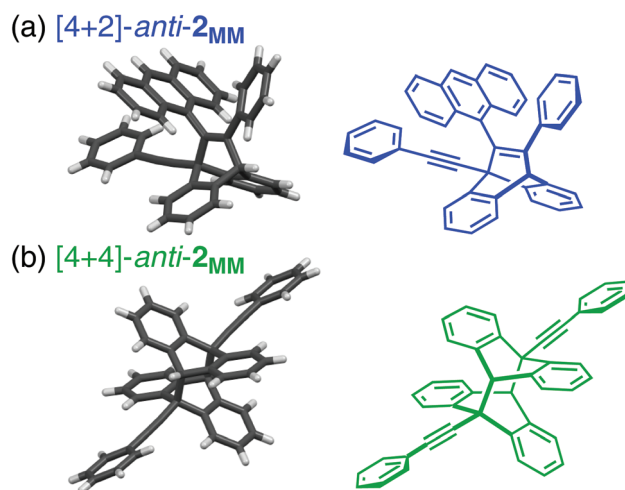


Fig. 4 The crystal structures of (a) [4 + 2]-*anti*-2_{MM} (CCDC 1503775) and (b) [4 + 4]-*anti*-2_{MM} (CCDC 1503774).

degassed benzene-*d*₆, affording [4 + 2]-*anti*-2_{MM} (80%) and [4 + 4]-*anti*-2_{MM} (15%) after 45 min irradiation (run 8 in Table 1 and Fig. S14†). The regioisomer ratio (5.3) was different from that reported by Becker and Andersson (9.4), but the difference may not be important.

The effects of oxygen, solvent (CDCl₃ and benzene-*d*₆) and concentration (0.50 and 8.0 mM) on the photooxidation and regioselectivity ([4 + 2]/[4 + 4]) during the photoreaction of **1_M** were further investigated at 25 °C and the results are summarised in Table 1. In dilute undegassed solution, the photooxidation of **1_M** preferentially took place more than that in the concentrated solution. In particular, irradiation of a dilute solution of **1_M** (0.50 mM) in undegassed CDCl₃ (run 1 in Table 1) quantitatively produced **1_M**-O₂ due to the heavy-atom effect of the solvent, which inhibits the photodimerisation by promoting intersystem crossing.^{12c} Although the concentration and solvent effects of the photodimerisation on regioselectivity were not significant, the yield of the major product, [4 + 2]-



anti-2_{MM}, tended to increase with the increasing concentration of **1_M** from 0.50 to 8.0 mM on changing the solvent from CDCl₃ to benzene-*d*₆.

We then calculated the structures of four possible photodimers (Fig. 1b) using the density functional theory (DFT) and found that their stabilities decrease in the following order: [4 + 2]-*anti-2_{MM}* > [4 + 2]-*syn-2_{MM}* > [4 + 4]-*anti-2_{MM}* > [4 + 4]-*syn-2_{MM}* (Fig. S5†), thus supporting the experimental results that the major product, [4 + 2]-*anti-2_{MM}*, is much more stable than the minor one, [4 + 4]-*anti-2_{MM}*, by 170.6 kJ mol⁻¹, whereas the corresponding *syn*-photodimers ([4 + 2]-*syn-2_{MM}* and [4 + 4]-*syn-2_{MM}*) could not be observed at all in the ¹H NMR spectra under the present conditions even though the *syn*-Diels–Alder adduct, [4 + 2]-*syn-2_{MM}*, is the second most stable photodimer. The reason is not clear, but it was suggested that it was due to the more favourable centrosymmetric-oriented complex formation ((**1_M**)₂), which could generate [4 + 2]-*syn-2_{MM}*,¹³ or these may be thermally unstable and immediately revert to the parent **1_M** in solution.

On the other hand, an energetically unfavourable [4 + 4]-*syn-2_{MM}* derivative was reported to form in a highly regioselective fashion on self-assembled flat metal surfaces upon photoirradiation (Fig. 1c) as revealed by STM,^{14a} Raman^{14b} and the time-dependent absorption spectral changes.¹⁵

Fig. S15† shows the experimental (top) and DFT simulated (bottom) Raman spectra of **1_M**, **1_M**-O₂, [4 + 2]-*anti-2_{MM}* and [4 + 4]-*anti-2_{MM}*, which are in good agreement, although **1_M**-O₂ contains **1_M** generated from **1_M**-O₂ via thermolysis (Fig. S15b†).

The peaks due to the anthracene residue of **1_M** completely disappeared in the Raman spectrum of [4 + 4]-*anti-2_{MM}* (Fig. S15d†), while these remained in the Raman spectrum of [4 + 2]-*anti-2_{MM}* (Fig. S15c†). Similar distinct spectral changes were also observed in the absorption spectra of **1_M**, [4 + 2]-*anti-2_{MM}* and [4 + 4]-*anti-2_{MM}* (Fig. S2a†). We note, however, that the Raman spectra of **1_M**-O₂ and [4 + 4]-*anti-2_{MM}*, in which an anthracene moiety no longer exists, were quite similar to each other except for a weak peak at 921 cm⁻¹ observed for **1_M**-O₂, which can be assigned to the –O–O– bond vibration

(Fig. S15b†).¹⁸ These results combined with the absorption spectra of **1_M**-O₂ and [4 + 4]-*anti-2_{MM}* (Fig. S2a†) suggested that it might be difficult to assign the photochemical reaction products of **1_M** and its derivatives, **1_M**-O₂ or [4 + 4]-*anti-2_{MM}*, based on the Raman^{14b} and absorption spectroscopies.¹⁵ However, it is apparent that the photooxidation is protected in the absence of oxygen.

Template effects on the photoreactions of mono-9-phenylethynylanthracene-bound carboxylic acid monomer

The mono-9-phenylethynylanthracene-bound carboxylic acid monomer (**1_C**) used in this study contains a 9-phenylethynylanthracene moiety identical to **1_M**, probably showing a similar photoreactivity to **1_M** in the absence of the template. Based on the photoreaction results of the model monomer **1_M** (Table 1), we employed a dilute CDCl₃ (0.50 mM) solution throughout the following photoreactions. As anticipated, the irradiation of **1_C** in undegassed CDCl₃ at 25 °C (run 1 in Table 2) resulted in the formation of endoperoxide (**1_C**-O₂)¹⁹ in 89% yield after 3 min as evidenced by the bridge-head proton (H_b) that newly appeared as a singlet at 6.08 ppm (Fig. 5a and S16a†); the chemical shift was very similar to that of **1_M**-O₂ (Fig. 3a and S6a†). The structure of **1_C**-O₂ was characterised and identified by comparing the ¹H NMR spectrum of **1_C**-O₂ with that of **1_M**-O₂ (Fig. S1†) and ESI-mass measurements (Fig. S16c†).

The photoreactions of **1_C** (0.50 mM) in the presence of the template **T_{AA}** (0.25 mM) and its monomeric amidine **A** (0.50 mM)²⁰ were then investigated in undegassed CDCl₃ at 25 °C. The monomeric amidine **A** was used for the control experiment to evaluate the template effect of **T_{AA}** on the photoreaction. The ¹H NMR spectra of **1_C** (0.50 mM) in the presence of **A** (0.50 mM) or **T_{AA}** (0.25 mM) showed the characteristic peaks for the NH protons in the low magnetic field at *ca.* 13.3 ppm, indicating the salt bridge formation (Fig. S18a and S19a†).

The irradiation of **A**·**1_C** (run 2 in Table 2) also produced only one set of ¹H NMR signals, such as H_b (6.09 ppm), resulting from the preferential formation of **1_C**-O₂ complexed with **A**

Table 2 Results of photoreactions of **1_C**

Run	1_C			Conv. (%) (consumption rate 10 ⁻³ k (s ⁻¹))	Product yield (%) (reaction rate 10 ⁻³ k (s ⁻¹))				Sup. Fig. no.
	Additive (conc. (mM))	Solvent (conc. (mM))	Irradiation time (min)		1_C -O ₂	[4 + 2]- <i>anti-2_{CC}</i>	[4 + 4]- <i>anti-2_{CC}</i>	[4 + 2]/ [4 + 4]	
1	—	Undegassed CDCl ₃ (0.50)	3	89 (11)	89 (11)	—	—	—	Fig. S16
2	A (0.50)	Undegassed CDCl ₃ (0.50)	3	89 (10)	89 (10)	—	—	—	Fig. S18
3	T_{AA} (0.25)	Undegassed CDCl ₃ (0.50)	2	92 (25)	10 ^a (4.4)	63 (11)	18 (2.5)	3.5	Fig. S19–20
4	—	Degassed CDCl ₃ (0.50)	60	85 (0.66)	—	60 (0.40)	25 (0.11)	2.4	Fig. S21
5	A (0.50)	Degassed CDCl ₃ (0.50)	90	68 (0.18)	—	19 (—) ^b	17 (0.036)	1.1	Fig. S22–24
6	T_{AA} (0.25)	Degassed CDCl ₃ (0.50)	2	89 (20)	—	68 (12)	20 (2.9)	3.4	Fig. S25–26

^a **1_C**-O₂ formed during the initial stage was gradually converted into an unknown compound probably due to photolysis products of **1_C**-O₂ upon further photoirradiation. The reaction rate was therefore estimated based on the time–conversion relationship during the initial stage. The maximum yield of **1_C**-O₂ was 10% after 30 s irradiation of light (>400 nm) (see Fig. S19a). ^b The peaks for (**A**)₂[4 + 2]-*anti-2_{CC}* were too broad to estimate its reaction rate (see Fig. S22a).



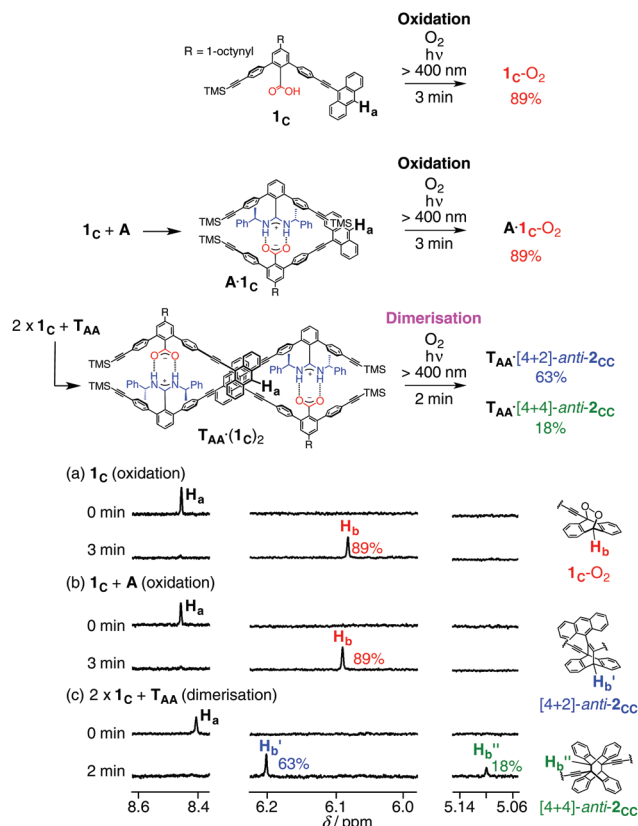


Fig. 5 Partial ^1H NMR (500 MHz, undegassed CDCl_3 , 25 $^\circ\text{C}$) spectra of 1_{C} (0.50 mM) in the absence (run 1 in Table 2) (a) and presence of A (0.50 mM) (run 2 in Table 2) (b) and T_{AA} (0.25 mM) (run 3 in Table 2) (c) before (top) and after (bottom) irradiation of light (>400 nm). Full-scale spectra are shown in Fig. S16a, S18a and S19a \dagger .

(Fig. 5b and S18a \dagger) as observed in the photooxidation of 1_{C} in the absence of A (run 1 in Table 2). In sharp contrast, upon the irradiation of $\text{T}_{\text{AA}}(1_{\text{C}})_2$ (run 3 in Table 2), the peak intensity of H_{a} decreased and almost disappeared within 2 min, whereas two new sets of singlet peaks due to the bridge-head protons (H'_{b} and H''_{b}) appeared at 6.21 and 5.10 ppm, respectively (Fig. 5c and S19a \dagger). These peaks could be clearly identified as the complexes of $\text{T}_{\text{AA}}[4+2]\text{-anti-2}_{\text{CC}}$ (63%) and $\text{T}_{\text{AA}}[4+4]\text{-anti-2}_{\text{CC}}$ (18%) based on the ^1H NMR spectra of the 1:1 mixtures of the isolated $[4+2]\text{-anti-2}_{\text{CC}}$ and $[4+4]\text{-anti-2}_{\text{CC}}$ after purification with T_{AA} , respectively (Fig. S28 \dagger). Interestingly, the photooxidation reaction of 1_{C} was significantly protected in the presence of the template T_{AA} , affording 1_{C}-O_2 in less than 10% yield (Fig. S19a \dagger) and the intermolecular photodimerisation selectively proceeded due to the close proximity of the two anthracene moieties arranged along the template, as supported by the decrease and red-shift of the absorption peaks of 1_{C} upon the addition of T_{AA} , indicative of the π -stacked arrangements of the anthracene moieties (Fig. S20 \dagger).

In the same way, the photoreactions of 1_{C} (0.50 mM) in the absence and presence of A (0.50 mM) or T_{AA} (0.25 mM) were performed in degassed CDCl_3 at 25 $^\circ\text{C}$ (runs 4–6 in Table 2), in

which the photooxidation was completely prohibited as observed in the model reaction of 1_{M} under the same conditions. In the absence of A and T_{AA} , 1_{C} was gradually converted to the photodimers, producing $[4+2]\text{-anti-2}_{\text{CC}}$ and $[4+4]\text{-anti-2}_{\text{CC}}$ in 60 and 25% yields, respectively, after irradiation for 60 min (run 4 in Table 2 and Fig. 6a and S21a \dagger).

Quite interestingly, the photodimerisation of 1_{C} in the presence of the template T_{AA} (run 6 in Table 2) took place much faster than that in the absence of T_{AA} , affording the $\text{T}_{\text{AA}}[4+2]\text{-anti-2}_{\text{CC}}$ (68%) and $\text{T}_{\text{AA}}[4+4]\text{-anti-2}_{\text{CC}}$ (20%) complexes after 2 min of light irradiation (Fig. 6c and S25a \dagger).²¹ Contrary to our expectation, however, we could not observe a specific regioselectivity during the photodimerisation, producing photodimers with an almost similar regioselectivity ($[4+2]/[4+4]$) to that in the absence of the template T_{AA} .

To estimate the reaction rate constant (k) of 1_{C} , the conversions of 1_{C} were estimated from the integral ratios of the peaks for H_{a} ($\text{T}_{\text{AA}}(1_{\text{C}})_2$), H'_{b} ($[4+2]\text{-anti-2}_{\text{CC}}$), H''_{b} ($[4+4]\text{-anti-2}_{\text{CC}}$) and the internal standard (1,1,2,2-tetrachloroethane) based on

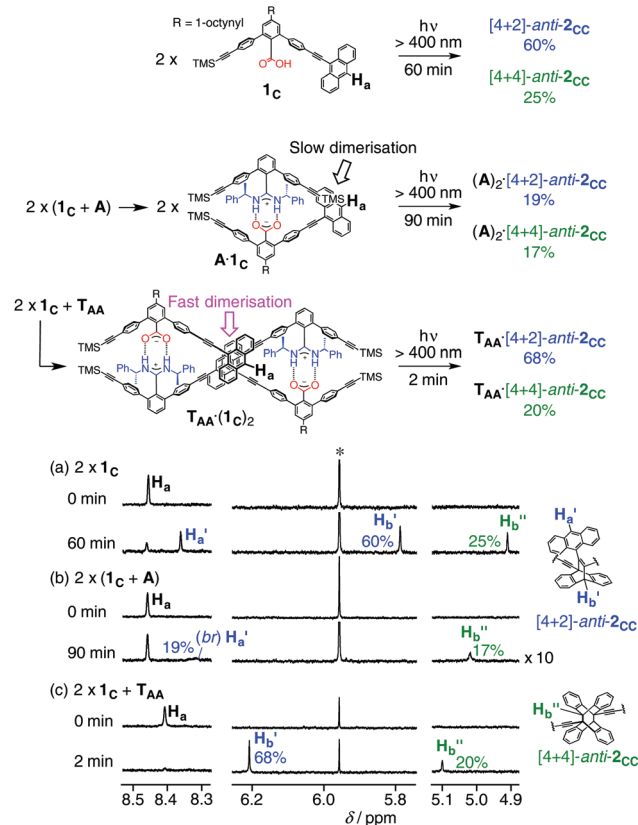


Fig. 6 Partial ^1H NMR (500 MHz, degassed CDCl_3 , 25 $^\circ\text{C}$) spectra of 1_{C} (0.50 mM) in the absence (run 4 in Table 2) (a) and presence of A (0.50 mM) (run 5 in Table 2) (b) and T_{AA} (0.25 mM) (run 6 in Table 2) (c) before (top) and after (bottom) irradiation of light (>400 nm). * denotes the peak due to 1,1,2,2-tetrachloroethane used as an internal standard. Full-scale spectra are shown in Fig. S21a, S22a and S25a \dagger . The peaks for $(\text{A})_2[4+2]\text{-anti-2}_{\text{CC}}$ were too broad to estimate its yield. The yield of $(\text{A})_2[4+2]\text{-anti-2}_{\text{CC}}$ was estimated to be 19% from the integral ratios of the peaks for isolated $[4+4]\text{-anti-2}_{\text{CC}}$ and $[4+2]\text{-anti-2}_{\text{CC}}$ (see Fig. S22b \dagger).



the ^1H NMR spectral changes and were plotted *versus* the reaction time (Fig. 7, S21, S23 and S25[†]). The experimental data were then fitted to a first-order kinetic model using eqn (1),

$$\ln(C/C_0) = -kt \quad (1)$$

where C is the concentration of 1_{C} , and t is the reaction time. As shown in Fig. 7, the photodimerisation was significantly accelerated in the presence of T_{AA} probably because of the close proximity of the anthracene moiety of 1_{C} along the template (Fig. S26[†]). The k values in the presence and absence of T_{AA} were then estimated to be $20 \times 10^{-3} \text{ s}^{-1}$ and $0.66 \times 10^{-3} \text{ s}^{-1}$, respectively, by the least-squares curve fitting method as shown in Fig. 7. Thus, the photodimerisation of 1_{C} was remarkably accelerated 30-fold ($k(\text{T}_{\text{AA}}(1_{\text{C}})_2)/k(1_{\text{C}}) = 30$) in the presence of T_{AA} through the salt bridges, although the tem-

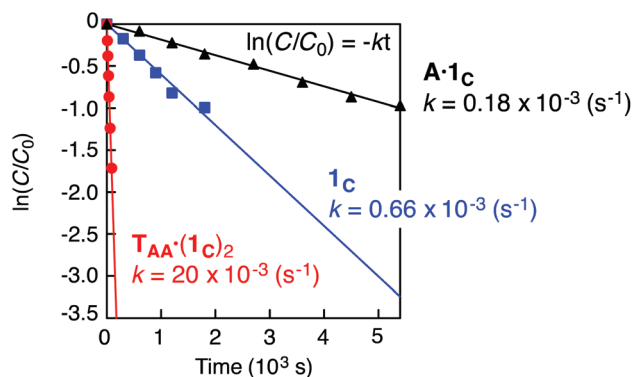


Fig. 7 Kinetic plots of the photodimerisation of 1_{C} (0.50 mM) in degassed CDCl_3 at $25\text{ }^\circ\text{C}$ in the absence (blue line) and presence of A (black line) and T_{AA} (red line). The reaction rates were estimated from the integral ratios of the peaks for H_a (1_{C}) and the internal standard (1,1,2,2-tetrachloroethane) based on the ^1H NMR spectral changes shown in Fig. S21a, S22a and S25a.[†]

plate-directed regioselectivity control during the photoreaction was not achieved.

In the presence of A , however, the photodimerisation (run 5 in Table 2) of 1_{C} took place very slowly with the k value of $0.18 \times 10^{-3} \text{ s}^{-1}$ (Fig. 7 and S23[†]). The ^1H NMR spectrum of $\text{A}\cdot 1_{\text{C}}$ after irradiation for 90 min was rather complicated except for the signals of $(\text{A})_2[4+4]\text{-anti-}2_{\text{CC}}$ (17%), and those of $(\text{A})_2[4+2]\text{-anti-}2_{\text{CC}}$ were not clearly observed because the signals were too broad (Fig. 6b and S22a[†]). The resulting photodimers with carboxylic acid residues were then isolated from the reaction mixture by silica gel column chromatography and the yield of $(\text{A})_2[4+2]\text{-anti-}2_{\text{CC}}$ was estimated to be 19% based on the integral ratio ($[4+2]\text{-anti-}2_{\text{CC}}/[4+4]\text{-anti-}2_{\text{CC}}$) in the ^1H NMR spectrum (Fig. S22b[†]). Molecular mechanics (MM) calculations for the $\text{A}\cdot 1_{\text{C}}$ salt-bridged complex suggested that one of the terminal TMS units of A is located close to the anthracene moiety of 1_{C} and a reactive acetylene residue of 1_{C} is likely sandwiched between the TMS and the phenyl group of the amidine residue of A (Fig. S24[†]). Thus, the photodimerisation of 1_{C} , in particular, the formation of $[4+2]\text{-anti-}2_{\text{CC}}$ may be considerably retarded once complexed with A due to such steric effects, leading to the decrease in the reaction rate.

Template effects on the photoreactions of di-9-phenylethynylantracene-bound carboxylic acid monomer

The photoreactions of the di-9-phenylethynylantracene-bound carboxylic acid monomer (3_{C}) (0.50 mM) in the absence and presence of the template T_{AA} (0.25 mM) were also investigated in undegassed and degassed CDCl_3 at $25\text{ }^\circ\text{C}$ (Table 3). The irradiation of 3_{C} in undegassed CDCl_3 (run 1 in Table 3 and Fig. S29[†]) readily promoted the photooxidation to produce a mixture of mono- (3_{C}-O_2) and di-endoperoxides ($3_{\text{C}}\text{-}2\text{O}_2$) in 50% yield as identified by the ESI-mass (Fig. S29c[†]) and NMR analysis (Fig. S1[†]), which eventually reverted to the parent 3_{C} and further converted in part to unknown compounds by

Table 3 Results of photoreactions of 3_{C}

Run	3_{C}	Additive (conc. (mM))	Solvent (conc. (mM))	Irradiation time (min)	Conv. (%) (consumption rate $10^{-3} k$ (s^{-1}))	Products yield (%) (reaction rate $10^{-3} k$ (s^{-1}))					Sup. Fig. no.	
						poly- 3_{C}		3_{C}-O_2 and $3_{\text{C}}\text{-}2\text{O}_2$	$[4+2]\text{-anti-}4_{\text{CC}}$	$[4+4]\text{-anti-}4_{\text{CC}}$		$[4+2]/[4+4]$
1	—	—	Undegassed CDCl_3	3	82 (9.9)	—	—				50 ^a (4.2)	
2	T_{AA}	(0.25)	Undegassed CDCl_3	2	97 (38)	—	—	12 (1.4)	60 ^b (19)	17 ^b (3.6)	3.5	Fig. S31–34
3	—	—	Degassed CDCl_3	60	22 ^c (0.61) ^c	72 ^d ($M_n = 3.2 \times 10^3$)	54 (0.39)	18 (0.010)	— ^e	— ^e	3.0	Fig. S35
4	T_{AA}	(0.25)	Degassed CDCl_3	2	95 (37)	—	—	74 (23)	20 (4)	3.7	—	Fig. S36–38

^a Total yield of mono- (3_{C}-O_2) and di-endoperoxides ($3_{\text{C}}\text{-}2\text{O}_2$) of 3_{C} , which were gradually converted into unknown compounds probably due to photolysis upon further photoirradiation (see Fig. S30). ^b One of the terminal anthracene units of $[4+2]\text{-}$ and $[4+4]\text{-anti-}4_{\text{CC}}$ was oxidised (see Fig. S31). ^c The conversion of 3_{C} and its consumption rate were estimated based on the formation of poly- 3_{C} using ^1H NMR (see Fig. S35a). ^d The number-average molecular weight (M_n) was determined by SEC using polystyrene standards in THF containing 0.1 wt% TBAB as the eluent (see Fig. 8B(a)). ^e It was difficult to estimate the yields of $[4+2]\text{-}$ and $[4+4]\text{-anti-}4_{\text{CC}}$ because their proton NMR signals were overlapped with those of poly- 3_{C} (see Fig. S35a).



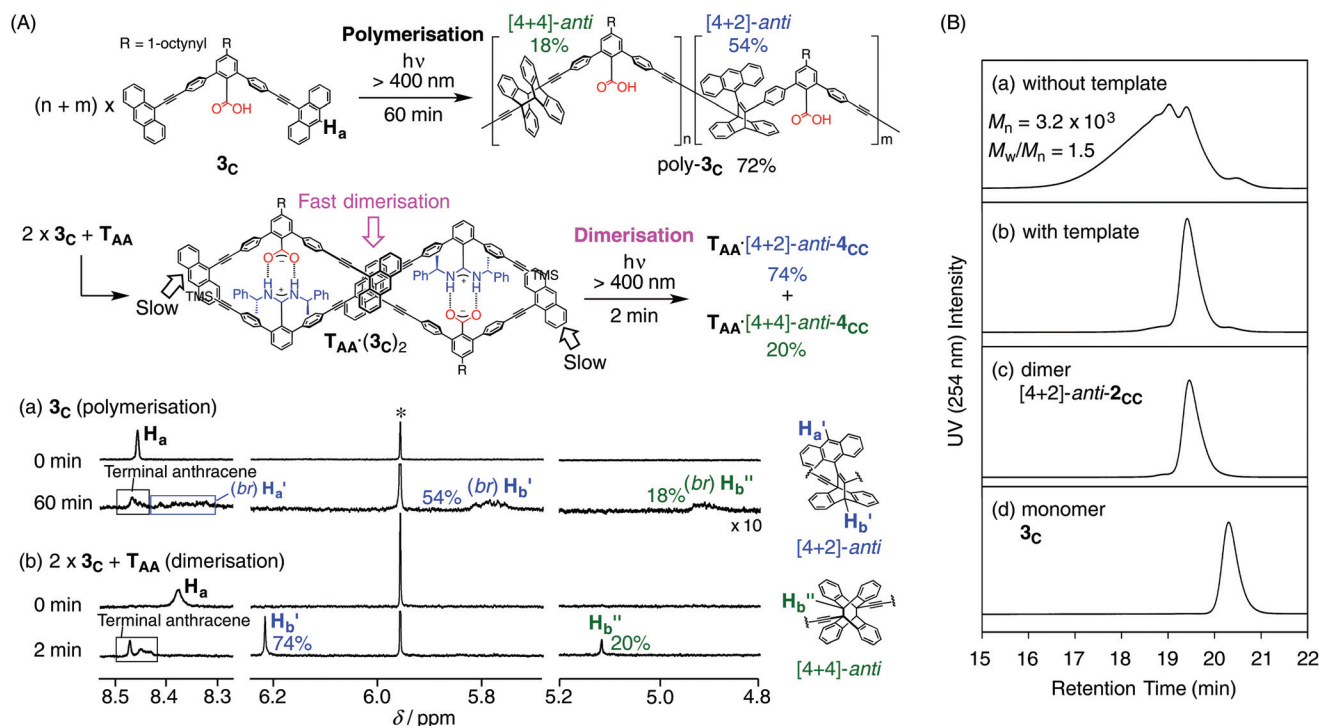


Fig. 8 (A) Partial $^1\text{H NMR}$ (500 MHz, degassed CDCl_3 , 25 °C) spectra of **3C** (0.50 mM) in the absence (run 3 in Table 3) (a) and presence of \mathbf{T}_{AA} (run 4 in Table 3) (b) before (top) and after (bottom) irradiation of light ($>400 \text{ nm}$). * denotes the peak due to 1,1,2,2-tetrachloroethane used as an internal standard. Full-scale spectra are shown in Fig. S35a and S36a.† (B) SEC chromatograms of (a) **poly-3C** produced in a degassed CDCl_3 solution of **3C** (0.50 mM) upon irradiation with light ($>400 \text{ nm}$) for 60 min (see Fig. S35†), (b) isolated carboxylic acid dimers obtained from $\mathbf{T}_{AA} \cdot (\mathbf{3C})_2$ (0.25 mM) after irradiation of light ($>400 \text{ nm}$) for 120 s in degassed CDCl_3 (see Fig. S37g†), (c) dimer $[4+2]\text{-anti-2}_{CC}$, and (d) monomer **3C**. These carboxylic acids were converted into the corresponding methyl esters by treatment with (trimethylsilyl)diazomethane before SEC analysis.

thermolysis (Fig. S30†). In the presence of \mathbf{T}_{AA} , the photooxidation of **3C** was significantly suppressed as anticipated (12% yield, run 2 in Table 3)²² and the $[4+2]\text{-}$ and $[4+4]\text{-anti-4}_{CC}$ photodimers were mainly produced in 60 and 17% yields, respectively, on the basis of the $^1\text{H NMR}$ spectra of the products by comparing them with those of the photodimers of **2_{CC}** formed in the presence of \mathbf{T}_{AA} (Fig. S37a–d†). We found that one of the terminal anthracene units of **4_{CC}** complexed with \mathbf{T}_{AA} was further oxidised (Fig. S31b†), resulting in the formation of the mono- and/or di-oxidised dimers, $[4+2]\text{-anti-4}_{CC}\text{-O}_2$ and $[4+4]\text{-anti-4}_{CC}\text{-O}_2$.

In strong contrast, the $^1\text{H NMR}$ spectrum of **3C** (0.50 mM) after irradiation for 60 min in degassed CDCl_3 (run 3 in Table 3) became significantly broadened, giving signals due to the $[4+2]\text{-}$ and $[4+4]\text{-anti}$ dimerisations (H'_b and H''_b), indicating the formation of a random copolymer (**poly-3C**) composed of $[4+2]\text{-}$ and $[4+4]\text{-anti}$ units (Fig. 8A(a) and S35a†). The size-exclusion chromatography (SEC) analysis further supported the polymerisation of **3C** (Fig. 8B(a)).²³ Interestingly, the photoreaction of $\mathbf{T}_{AA} \cdot (\mathbf{3C})_2$ in degassed CDCl_3 (run 4 in Table 3) showed two sharp bridge-head peaks (H'_b and H''_b), suggesting the formation of the photodimers, $\mathbf{T}_{AA} \cdot [4+2]\text{-anti-4}_{CC}$ and $\mathbf{T}_{AA} \cdot [4+4]\text{-anti-4}_{CC}$, while the other anthracene moieties remained unreacted as evidenced by the $^1\text{H NMR}$ and absorption spectra (Fig. 8A(b), S36a and S38†). The SEC analysis of the products further supported this conclusion (Fig. 8B(b–d)).

These results indicated that the dimeric template \mathbf{T}_{AA} selectively promoted the photodimerisation of the anthracene units of the bimolecular **3C** located in close proximity at the center (Fig. S38†), whereas the further polymerisation of the resultant $\mathbf{T}_{AA} \cdot [4+2]\text{-anti-4}_{CC}$ and $\mathbf{T}_{AA} \cdot [4+4]\text{-anti-4}_{CC}$ dimers was exclusively protected due to the steric effects between the remaining anthracene units at the ends and the TMS and phenyl groups of the amidine residues of \mathbf{T}_{AA} as observed in the photodimerisation of **A·1C** (run 5 in Table 2).

In the same way, the k values of **3C** in degassed CDCl_3 in the presence and absence of \mathbf{T}_{AA} were estimated to be $37 \times 10^{-3} \text{ s}^{-1}$ and $0.61 \times 10^{-3} \text{ s}^{-1}$, respectively, (Fig. S35d and S36c†). Thus, the photodimerisation of **3C** was accelerated 61-fold ($k(\mathbf{T}_{AA} \cdot (\mathbf{3C})_2)/k(\mathbf{3C}) = 61$) in the presence of \mathbf{T}_{AA} . Moreover, the dimerisation of **3C** was found to take place faster than that of **1C** in the presence of \mathbf{T}_{AA} by a factor of 1.9 ($k(\mathbf{T}_{AA} \cdot (\mathbf{3C})_2)/k(\mathbf{T}_{AA} \cdot (\mathbf{1C})_2) = 1.9$). This indicated that **3C** can more effectively dimerise along the template than **1C** because **3C** possesses two anthracene moieties at both ends (Fig. S37e†).

Conclusions

In conclusion, we have performed a close inspection of the photochemical reactions of 9-phenylethynylantracene under



various reaction conditions and proved the [4 + 4]-*anti* and [4 + 2]-*anti* dimers structures produced during the photodimerisation¹³ by single-crystal X-ray analysis. We also found a remarkable template effect of the amidine dimer on the photo-reactions of the mono- and di-9-phenylethynylanthracene-bound carboxylic acid monomers. The detailed kinetic and structural studies revealed that the [4 + 4]- and [4 + 2]-*anti* photodimers (**2_{CC}** and **4_{CC}**) were selectively produced along the template and the reaction rate was accelerated 30 or 61-fold without side reactions, oxidation and polymerisation. The observed noticeable enhancement of the dimerisation rate constants could be ascribed to the two anthracene moieties of the monomers located in close proximity at the reaction site along the rigid template assisted by the amidinium-carboxylate salt bridges. Although the template-directed, specific regioselective-photodimerisation was not achieved, the present template-directed photodimerisation system based on salt bridges will be further applied to the template-directed enantioselective photodimerisation of prochiral anthracene derivatives^{10,24} because the amidine dimer used in the present study is optically active.²⁵ Studies along this line are now underway in our laboratory.

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- 19 The photooxidised 1_{C}-O_2 gradually decomposed under shielded light, producing the monomer 1_{C} together with a small amount of an unknown compound (Fig. S17†).
- 20 The association constant (K_{a}) between 1_{C} and A could be roughly estimated to be $ca. 3.5 \times 10^6 \text{ M}^{-1}$ in CDCl_3 by comparison of the K_{a} value between analogous amidine and carboxylic acids.¹⁶
- 21 The template T_{AA} possesses four alkyne units that are not bonded to the anthracene residue. However, these alkyne units did not participate in the photoreactions because the conversion (89%) of 1_{C} after photoirradiation for 2 min in the presence of T_{AA} is almost consistent with the total yield (68 and 20%) of the resulting carboxylic acid photodimers ([4 + 2]-anti- 2_{CC} and [4 + 4]-anti- 2_{CC}) (run 6 in Table 2). In addition, the structures of the dimer products isolated were fully characterised, indicating that the photodimers were not composed of T_{AA} at all. Becker and Andersson also reported that the intermolecular photodimerisation between anthracene and diphenylacetylene did not take place, giving no [4 + 2]-cycloadduct upon light irradiation over 400 nm.¹³ This also suggests that the alkyne units of T_{AA} will not react with the anthracene unit(s) of 1_{C} and 3_{C} upon photoirradiation (>400 nm).
- 22 The peak assignments were performed by comparing the ^1H NMR spectrum of a mixture of 3_{C}-O_2 and 3_{C}-2O_2 in the presence of T_{AA} (Fig. S33†).



- 23 Poly-3_C was converted to the corresponding methyl esters by treatment with (trimethylsilyl)diazomethane. The number average molecular weight (M_n) and its distribution (M_w/M_n) were estimated to be 3.2×10^3 and 1.5, respectively, by SEC using polystyrene standards and THF containing 0.1 wt% tetrabutylammonium bromide as the eluent. The M_n value corresponds to *ca.* 4 repeating units in a single polymer chain.
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- 25 The complexes of the achiral 1_C and 3_C with the optically active amidine template T_{AA} exhibited apparent Cotton effects in the absorption region of the anthracene residues (*ca.*, 350–440 nm) accompanied by a decrease and red-shift in their absorption spectra (Fig. S20, S26, S34 and S38†), indicating that the two anthracene units of the monomers appear to be arranged in a chiral fashion along the chiral template. These results seem to be promising for realising such a template-directed enantioselective photodimerisation.

