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

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

Junki Tanabe, Daisuke Taura, Naoki Ousaka and Eiji Yashima*

The photoirradiation of 9-phenylethynylanthracene 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-phenylethynylanthracene 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-phenylethynylanthracene-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-phenylethynylanthracene-bound monomer was preferentially photo-polymerised in the absence of the template.

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-

et 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 cyclo-
dextrins3f,10 and cucurbit[n]urils,5d,e,11f,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-
dextrin\textsuperscript{37,10} and in the crystal state\textsuperscript{12c} even in the presence of oxygen.

Becker and Andersson reported that the irradiation of 9-phenylethynylanthracene (1\textsubscript{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 1\textsubscript{M} over the [4 + 4] cycloaddition reaction, predominantly producing a [4 + 2]-anti dimer ([4 + 2]-anti-2\textsubscript{MM}, Fig. 1b).\textsuperscript{13} In contrast, Weiss and co-workers demonstrated the energetically unfavourable [4 + 4]-syn dimer formation of thiolated 9-phenylethynylanthracenes (1\textsubscript{M}-SH) (Fig. 1c) upon irradiation that proceeded in a highly regioselective manner when 1\textsubscript{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-2\textsubscript{MM}) could be possible.\textsuperscript{14} The regioselective [4 + 4]-syn dimer formation was monitored by scanning tunneling microscopy (STM)\textsuperscript{14a} and surface-enhanced Raman spectroscopy (SERS),\textsuperscript{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 1\textsubscript{M}-SH immobilised on metallic (Au and Pd) nanoparticles dimerised in a regioselective way to yield a [4 + 4]-syn cycloaddition product under photo-irradiation (Fig. 1c), based on the time-dependent absorption spectral changes.\textsuperscript{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 directional property even in polar solvents.\textsuperscript{16} Therefore, various types of functional linkers, such as Pt(n)-acetylide\textsuperscript{16b,d,f,j,l,p} and azobenzene linkages,\textsuperscript{16d,f,i,m} can be introduced between the m-terphenyl units while maintaining the double-helical structures.\textsuperscript{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.\textsuperscript{16i,n} 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 (1\textsubscript{C} and 3\textsubscript{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 (T\textsubscript{AA}) connected by a p-diyethynylbenzene unit as the template (Fig. 2d). The monomers 1\textsubscript{C} and 3\textsubscript{C} possess one or two 9-phenylethynylanthracene moieties identical to 1\textsubscript{M}, hence we anticipated the regioselective photodimerisation or polymerisation of 1\textsubscript{C} or 3\textsubscript{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 T\textsubscript{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 1\textsubscript{M} (Fig. 1b),\textsuperscript{13} a model compound of 1\textsubscript{C} and 3\textsubscript{C}, was also thoroughly investigated under various conditions. We found that a [4 + 4]-anti-dimer ([4 + 4]-anti-2\textsubscript{MM}) was also produced as a minor product along with the major Diels–Alder addition product, [4 + 2]-anti-2\textsubscript{MM}, (Fig. 1b) and then their structures were unambiguously determined by single-crystal X-ray analysis.

### Results and discussion

#### Synthesis

9-Phenylethynylanthracene (1\textsubscript{M}) was prepared according to the reported method.\textsuperscript{17} The achiral carboxylic acid monomers (1\textsubscript{C} and 3\textsubscript{C}) bearing an anthracene group at one and both ends were newly synthesised according to Schemes S3 and S5, respectively, (see the ES\textsuperscript{†}). The p-phenylene-linked optically active amidine dimer (T\textsubscript{AA})\textsuperscript{16i} and its monomeric amidine (A)\textsuperscript{16a} were also prepared according to the reported methods.

#### Photoreactions of model monomer (1\textsubscript{M})

The photoreaction of 1\textsubscript{M} (0.50 mM) was first investigated in undegassed CDCl\textsubscript{3} at 25 °C (run 1 in Table 1) upon light...
irradiation over 400 nm. Reaction progress was monitored by $^1$H NMR spectroscopy. The peak intensity of the anthracene proton ($H_a$) at the 10-position in $^{1M}$ 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 ($^{1M}$-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 $m/z = 309.19$ ($^{1M}$-O$_2$–H$^-$) in its negative-mode electron-spray ionisation (ESI) mass spectrum of the reaction mixture and also by the absorption spectrum of $^{1M}$ after irradiation for 3 min, in which the peaks due to the anthracene moiety almost disappeared (Fig. S6†). It was noted that the obtained $^{1M}$-O$_2$ was not stable in solution and was thermally converted back to $^{1M}$ without decomposition at 25 °C.$^{12,b,d,f}$ 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 $^1$H NMR spectral changes (Fig. S7†).

In contrast, after light irradiation of $^{1M}$ (0.50 mM) for 30 min in degassed CDCl$_3$ at 25 °C (run 5 in Table 1), the $^1$H 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
photodimers (Fig. 3b and S11a†), which were unambiguously identified as [4 + 2]-anti-2MM and [4 + 4]-anti-2MM, 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 1M (8.0 mM) in degassed benzene gave [4 + 2]-anti-2MM 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 1M (8.0 mM) under almost the same conditions in degassed benzene-d$_6$, affording [4 + 2]-anti-2MM (80%) and [4 + 4]-anti-2MM (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 (CDCl$_3$ 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 1M were further investigated at 25 °C and the results are summarised in Table 1. In dilute undegassed solution, the photooxidation of 1M preferentially took place more than that in the concentrated solution. In particular, irradiation of a dilute solution of 1M (0.50 mM) in undegassed CDCl$_3$ (run 1 in Table 1) quantitatively produced 1M-O$_2$ due to the heavy-atom effect of the solvent, which inhibits the photodimerisation by promoting intersystem crossing. 12 Although the concentration and solvent effects of the photodimerisation on regioselectivity were not significant, the yield of the major product, [4 + 2]-

### Table 1

Results of photoreactions of 1M under various reaction conditions

<table>
<thead>
<tr>
<th>Run</th>
<th>Solvent (conc. (mM))</th>
<th>Irradiation time (min)</th>
<th>Conv. (%)</th>
<th>Product yield (%) (Reaction rate 10$^{-3}$ k (s$^{-1}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Undegassed CDCl$_3$ (0.50)</td>
<td>3</td>
<td>89 (16)</td>
<td>1M-O$_2$ [4 + 2]-anti-2MM [4 + 4]-anti-2MM [4 + 2]/[4 + 4] Sup. Fig. no.</td>
</tr>
<tr>
<td>2</td>
<td>Undegassed CDCl$_3$ (8.0)</td>
<td>30</td>
<td>88 (2.0)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Undegassed benzene-d$_6$ (0.50)</td>
<td>16</td>
<td>88 (3.2)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Undegassed benzene-d$_6$ (8.0)</td>
<td>30</td>
<td>96 (1.9)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Degassed CDCl$_3$ (0.50)</td>
<td>30</td>
<td>88 (1.7)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Degassed CDCl$_3$ (8.0)</td>
<td>45</td>
<td>95 (1.5)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Degassed benzene-d$_6$ (0.50)</td>
<td>30</td>
<td>90 (1.6)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Degassed benzene-d$_6$ (8.0)</td>
<td>45</td>
<td>97 (1.3)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Degassed benzene (8.0)</td>
<td>90</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

The maximum yield of 1M-O$_2$ was 18% after 8 min irradiation of light (>400 nm) (see Fig. S8a). The maximum yield of 1M-O$_2$ was 38% after 8 min irradiation of light (>400 nm) (see Fig. S9a). The maximum yield of 1M-O$_2$ was 15% after 8 min irradiation of light (>400 nm) (see Fig. S10a). Not available in ref. 13.

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**Fig. 3** Partial $^1$H NMR (500 MHz, 25 °C) spectra of 1M (0.50 mM) in (a) (run 1 in Table 1) undegassed and (b) (run 5 in Table 1) degassed CDCl$_3$ before (top) and after (bottom) irradiation of light (>400 nm). Full-scale spectra are shown in Fig. S6a and S11a† respectively.

**Fig. 4** The crystal structures of (a) [4 + 2]-anti-2MM (CCDC 1503775) and (b) [4 + 4]-anti-2MM (CCDC 1503774).
anti-2-MM tended to increase with the increasing concentration of 1M from 0.50 to 8.0 mM on changing the solvent from CDCl₃ to benzene-d₆.

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. S5f), 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 ([1M]₂), which could generate [4 + 2]-syn-2-MM.² or these may be thermally unstable and immediately revert to the parent 1M 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 photoradiation (Fig. 1c) as revealed by STM,¹⁶e Ramam¹⁴b and the time-dependent absorption spectral changes.¹⁵

Fig. S15f shows the experimental (top) and DFT simulated (bottom) Raman spectra of 1M, 1M-O₂, [4 + 2]-anti-2-MM and [4 + 4]-anti-2-MM, which are in good agreement, although 1M-O₂ contains 1M generated from 1M-O₂ via thermolysis (Fig. S15fb).

The peaks due to the anthracene residue of 1M completely disappeared in the Raman spectrum of [4 + 4]-anti-2-MM (Fig. S15fd), while these remained in the Raman spectrum of [4 + 2]-anti-2-MM (Fig. S15cf). Similar distinct spectral changes were also observed in the absorption spectra of 1M, [4 + 2]-anti-2-MM and [4 + 4]-anti-2-MM (Fig. S2af). We note, however, that the Raman spectra of 1M-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 1M-O₂, which can be assigned to the –O–O– bond vibration (Fig. S15fb).¹⁸ These results combined with the absorption spectra of 1M-O₂ and [4 + 4]-anti-2-MM (Fig. S2af) suggested that it might be difficult to assign the photochemical reaction products of 1M and its derivatives, 1M-O₂ or [4 + 4]-anti-2-MM, based on the Raman¹⁴b 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 1C used in this study contains a 9-phenylethynylanthracene moiety identical to 1M, probably showing a similar photoactivity to 1M in the absence of the template. Based on the photoreaction results of the model monomer 1M (Table 1), we employed a dilute CDCl₃ (0.50 mM) solution throughout the following photoreactions. As anticipated, the irradiation of 1C in undegassed CDCl₃ at 25 °C (run 1 in Table 2) resulted in the formation of endoperoxide (1C-O₂)¹⁹ in 89% yield after 3 min as evidenced by the bridge-head proton (H₆) that newly appeared as a singlet at 6.08 ppm (Fig. 5a and S16af); the chemical shift was very similar to that of 3M-O₂ (Fig. 3a and S6at). The structure of 1C-O₂ was characterised and identified by comparing the ¹H NMR spectrum of 1C-O₂ with that of 1M-O₂ (Fig. S17f) and ESI-mass measurements (Fig. S16ct).

The photoreactions of 1C (0.50 mM) in the presence of the template TAA (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 TAA on the photoreaction. The ¹H NMR spectra of 1C (0.50 mM) in the presence of A (0.50 mM) or TAA (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 S19at).

The irradiation of A-1C (run 2 in Table 2) also produced only one set of ¹H NMR signals, such as H₆ (6.09 ppm), resulting from the preferential formation of 1C-O₂ complexed with A.

### Table 2 Results of photoreactions of 1C

<table>
<thead>
<tr>
<th>Run</th>
<th>Additive (conc. [mM])</th>
<th>Solvent (conc. [mM])</th>
<th>Irradiation time (min)</th>
<th>Conv. (%)</th>
<th>Product yield (%) (reaction rate 10⁻³ k (s⁻¹))</th>
<th>Sup. Fig. no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>—</td>
<td>Undegassed CDCl₃ (0.50)</td>
<td>3</td>
<td>89 (11)</td>
<td>89 (11) – – –</td>
<td>Fig. S16</td>
</tr>
<tr>
<td>2</td>
<td>A (0.50)</td>
<td>Undegassed CDCl₃ (0.50)</td>
<td>3</td>
<td>89 (10)</td>
<td>89 (10) – – –</td>
<td>Fig. S18</td>
</tr>
<tr>
<td>3</td>
<td>TAA (0.25)</td>
<td>Undegassed CDCl₃ (0.50)</td>
<td>2</td>
<td>92 (25)</td>
<td>10 (4.4) 63 (11) 18 (2.5) 3.5</td>
<td>Fig. S19–20</td>
</tr>
<tr>
<td>4</td>
<td>—</td>
<td>Degassed CDCl₃ (0.50)</td>
<td>60</td>
<td>85 (0.66)</td>
<td>60 (0.40) 25 (0.11) 2.4</td>
<td>Fig. S21</td>
</tr>
<tr>
<td>5</td>
<td>A (0.50)</td>
<td>Degassed CDCl₃ (0.50)</td>
<td>90</td>
<td>68 (0.18)</td>
<td>19 (–) 17 (0.036) 1.1</td>
<td>Fig. S22–24</td>
</tr>
<tr>
<td>6</td>
<td>TAA (0.25)</td>
<td>Degassed CDCl₃ (0.50)</td>
<td>2</td>
<td>89 (20)</td>
<td>68 (12) 20 (2.9) 3.4</td>
<td>Fig. S25–26</td>
</tr>
</tbody>
</table>

* 1C-O₂ formed during the initial stage was gradually converted into an unknown compound probably due to photolysis products of 1C-O₂ upon further photoradiation. The reaction rate was therefore estimated based on the time-conversion relationship during the initial stage. The maximum yield of 1C-O₂ was 10% after 30 s irradiation of light (~400 nm) (see Fig. S19a).* The peaks for [A]₂[4 + 2]anti-2CC were too broad to estimate its reaction rate (see Fig. S22a).
with which the photooxidation was completely prohibited as observed in the model reaction of 1C under the same conditions. In the absence of A and TAA, 1C was gradually converted to the photodimers, producing \([4 + 2]-anti-2\text{CC}\) and \([4 + 4]-anti-2\text{CC}\) in 60 and 25% yields, respectively, after irradiation for 60 min (run 4 in Table 2 and Fig. 6a and S21a).

Quite interestingly, the photodimerisation of 1C in the presence of the template TAA (run 6 in Table 2) took place much faster than that in the absence of TAA, affording the TAA\([4 + 2]-anti-2\text{CC}\) (68%) and TAA\([4 + 4]-anti-2\text{CC}\) (20%) complexes after 2 min of light irradiation (Fig. 6c and S25a).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 TAA.

To estimate the reaction rate constant \((k)\) of 1C, the conversions of 1C were estimated from the integral ratios of the peaks for Ha \((\text{TAA}(1C)_2)\), H\text{″}b \([4 + 4]-anti-2\text{CC}\), H\text{″}b \([4 + 4]-anti-2\text{CC}\) and the internal standard \((1,1,2,2\text{-tetrachloroethane})\) based on

\[\text{Ha} \rightarrow \text{Ha}^* \rightarrow \text{Hb}^* \rightarrow \text{Hb} \rightarrow \text{Hb}^* \rightarrow \text{Hb}^* \rightarrow \text{Hb} \rightarrow \text{Hb}^* \rightarrow \text{Hb} \rightarrow \text{Hb} \]

(Fig. 5b and S18a) as observed in the photooxidation of 1C in the absence of A (run 1 in Table 2). In sharp contrast, upon the irradiation of TAA\(1C\) (run 3 in Table 2), the peak intensity of Ha decreased and almost disappeared within 2 min, whereas two new sets of singlet peaks due to the bridge-head protons (H\text{′}b and H\text{′}′b) appeared at 6.21 and 5.10 ppm, respectively (Fig. 5c and S19a). These peaks could be clearly identified as the complexes of TAA\([4 + 2]-anti-2\text{CC}\) (63%) and TAA\([4 + 4]-anti-2\text{CC}\) (18%) based on the \(^1\text{H} \text{NMR}\) spectra of the 1:1 mixtures of the isolated \([4 + 2]-anti-2\text{CC}\) and \([4 + 4]-anti-2\text{CC}\) after purification with TAA, respectively (Fig. S28).

Interestingly, the photooxidation reaction of 1C was significantly protected in the presence of the template TAA, affording 1C\( \cdot \text{O}_2\) in less than 10% yield (Fig. S19a) 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 1C upon the addition of TAA, indicative of the \(\pi\)-stacked arrangements of the anthracene moieties (Fig. S20).

In the same way, the photoreactions of 1C (0.50 mM) in the absence and presence of A (0.50 mM) or TAA (0.25 mM) were performed in degassed CDCl\(_3\) at 25 °C (runs 4–6 in Table 2), in
the $^1$H 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),

$$\ln(C/C_0) = -kt$$  \hspace{1cm} (1)

where $C$ is the concentration of $1C$, 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 $1C$ along the template (Fig. S26). The $k$ values in the presence and absence of $T_{AA}$ were then estimated to be $20 \times 10^{-3}$ s$^{-1}$ and $0.66 \times 10^{-3}$ s$^{-1}$, respectively, by the least-squares curve fitting method as shown in Fig. 7. Thus, the photodimerisation of $1C$ was remarkably accelerated 30-fold ($k(T_{AA}(1C))$/$k(1C) = 30$) in the presence of $T_{AA}$ through the salt bridges, although the template-directed regioselectivity control during the photoreaction was not achieved.

In the presence of $A$, however, the photodimerisation (run 5 in Table 2) of $1C$ took place very slowly with the $k$ value of $0.18 \times 10^{-3}$ s$^{-1}$ (Fig. 7 and S23f). The $^1$H NMR spectrum of $A$-$1C$ after irradiation for 90 min was rather complicated except for the signals of ($A$)$_2$-[4 + 4]-anti-2CC (17%), and those of ($A$)$_2$-[4 + 2]-anti-2CC 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 ($A$)$_2$-[4 + 2]-anti-2CC was estimated to be 19% based on the integral ratio ([3 + 2]anti-2CC/([4 + 4]-anti-2CC)) in the $^1$H NMR spectrum (Fig. S22bf). Molecular mechanics (MM) calculations for the A-$1C$ salt-bridged complex suggested that one of the terminal TMS units of $A$ is located close to the anthracene moiety of $1C$ and a reactive acetylene residue of $1C$ is likely sandwiched between the TMS and the phenyl group of the amidine residue of $A$ (Fig. S24f). Thus, the photodimerisation of $1C$, in particular, the formation of [4 + 2]-anti-2CC 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-phenylethynylantranence-bound carboxylic acid monomer**

The photoreactions of the di-9-phenylethynylantrancene-bound carboxylic acid monomer ($3C$) (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 °C (Table 3). The irradiation of $3C$ in undegassed CDCl$_3$ (run 1 in Table 3 and Fig. S29f) readily promoted the photooxidation to produce a mixture of mono-($3C$-O$_2$) and di-endoperoxides ($3C$-2O$_2$) in 50% yield as identified by the ESI-mass (Fig. S29cf) and NMR analysis (Fig. S1f), which eventually reverted to the parent $3C$ and further converted in part to unknown compounds by

![Fig. 7 Kinetic plots of the photodimerisation of $1C$ (0.50 mM) in degassed CDCl$_3$ at 25 °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 $H_4$ ($1C$) and the internal standard (1,1,2,2-tetrachloroethane) based on the $^1$H NMR spectral changes shown in Fig. S21a, S22a and S25a.](image)

**Table 3** Results of photoreactions of $3C$

<table>
<thead>
<tr>
<th>Run</th>
<th>Additive (conc. (mM))</th>
<th>Solvent (conc. (mM))</th>
<th>Irradiation time (min)</th>
<th>Conv. (%) (consumption rate $10^{-3}$ k (s$^{-1}$))</th>
<th>Products yield (%) (reaction rate $10^{-3}$ k (s$^{-1}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>poly-$3C$</td>
<td>[4 + 2]- anti</td>
</tr>
<tr>
<td>1</td>
<td>—</td>
<td>Undegassed CDCl$_3$</td>
<td>3</td>
<td>82 (9.9)</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>$T_{AA}$ (0.25)</td>
<td>Undegassed CDCl$_3$</td>
<td>2</td>
<td>97 (38)</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>—</td>
<td>Degassed CDCl$_3$</td>
<td>60</td>
<td>22 (0.61)*</td>
<td>72$^a$ M$_{av}$ = 3.2 $\times$ 10$^3$</td>
</tr>
<tr>
<td>4</td>
<td>$T_{AA}$ (0.25)</td>
<td>Degassed CDCl$_3$</td>
<td>2</td>
<td>95 (37)</td>
<td>74 (23)</td>
</tr>
</tbody>
</table>

$^a$Total yield of mono-($3C$-O$_2$) and di-endoperoxides ($3C$-2O$_2$) of $3C$, 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] and [4 + 4]-anti-4CC was oxidised (see Fig. S31).$^c$The conversion of $3C$ and its consumption rate were estimated based on the formation of poly-$3C$ using $^1$H 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] and [4 + 4]-anti-4CC because their proton NMR signals were overlapped with those of poly-$3C$ (see Fig. S35a).
thermolysis (Fig. S30†). In the presence of $T_{AA}$, the photooxidation of $3_C$ was significantly suppressed as anticipated (12% yield, run 2 in Table 3) and the [4 + 2]- and [4 + 4]-anti-4CC photo-dimers were mainly produced in 60 and 17% yields, respectively, on the basis of the $^1$H NMR spectra of the products by comparing with those of the photodimers of 2CC formed in the presence of $T_{AA}$ (Fig. S37a-d†). We found that one of the terminal anthracene units of 4CC complexed with $T_{AA}$ was further oxidised (Fig. S31b†), resulting in the formation of the mono- and/or di-oxidised dimers, [4 + 2]-anti-4CC-O$_2$ and [4 + 4]-anti-4CC-O$_2$.

In strong contrast, the $^1$H NMR spectrum of $3_C$ (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]- and [4 + 4]-anti dimerisations (H$^b_b$ and H$^b_e$), indicating the formation of a random copolymer (poly-3C) composed of [4 + 2]- and [4 + 4]-anti units (Fig. 8A(a) and S35a†). The size-exclusion chromatography (SEC) analysis further supported the polymerisation of 3C (Fig. 8B(a)). Interestingly, the photoreaction of $T_{AA} (3_C)_2$ in degassed CDCl$_3$ (run 4 in Table 3) showed two sharp bridge-head peaks (H$^b_b$ and H$^b_e$), suggesting the formation of the photodimers, $T_{AA} [4 + 2]$-anti-4CC and $T_{AA} [4 + 4]$-anti-4CC, while the other anthracene moieties remained unreacted as evidenced by the $^1$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 $T_{AA}$ 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 $T_{AA} [4 + 2]$-anti-4CC and $T_{AA} [4 + 4]$-anti-4CC 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 $T_{AA}$ 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 $T_{AA}$ were estimated to be 37 $\times$ 10$^{-3}$ s$^{-1}$ and 0.61 $\times$ 10$^{-3}$ s$^{-1}$, respectively, (Fig. S35d and S36ef†). Thus, the photodimerisation of 3C was accelerated 61-fold ($k(T_{AA} [3C]_2)/k(3C) = 61$) in the presence of $T_{AA}$. Moreover, the dimerisation of 3C was found to take place faster than that of 1C in the presence of $T_{AA}$ by a factor of 1.9 ($k(T_{AA} [3C]_2)/k(T_{AA} [1C]_2) = 1.9$). This indicated that 3C can more effectively dimerise along the template than 1C because 3C possesses two anthracene moieties at both ends (Fig. S37ef†).

Conclusions

In conclusion, we have performed a close inspection of the photochemical reactions of 9-phenylethynylanthracene under
various reaction conditions and proved the [4 + 4]-anti and [4 + 2]-anti dimers structures produced during the photodimerisation\textsuperscript{13} 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\textsubscript{CC} and 4\textsubscript{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 salt bridges. Although the template-directed, specific regioselective-photodimerisation was not achieved, the present study is optically active.\textsuperscript{25} Studies along this line are now underway in our laboratory.

Acknowledgements

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Notes and references


The peak assignments were performed by comparing the $^1$H NMR spectrum of a mixture of $[4 + 2]$-addition, the structures of the dimer products isolated 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-2cc and [4 + 4]-anti-2cc) (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]-cyloadduct upon light irradiation over 400 nm. This also suggests that the alkyne units of $T_{AA}$ will not react with the anthracene unit(s) of 1C and 3C upon photoirradiation (>400 nm).
23 Poly-3C 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 $3.2 \times 10^3$ 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.


25 The complexes of the achiral 1C and 3C with the optically active amidine template TAA 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.