# Complementarity in bimolecular photochromism†

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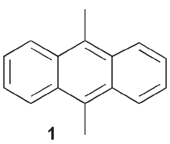
**Irradiating 2,3,6,7-tetraphenylanthracene in the presence of 9,10-dimethylanthracene leads to exclusive formation of the cross-dimer. No photochemical reaction is observed when either of these chromophores is irradiated in the absence of the other.**

Photochromism is perhaps one of the most powerful methods for reversibly altering molecular and macroscopic properties by the application of an external stimulus.[1] Indeed the ability to photochemically toggle molecules between two or more states has been exploited in contexts ranging from information storage[2,3] to enzyme activity modulation.[4,5] In the vast majority of cases, switching is brought about by the unimolecular isomerization of molecules such as azobenzene or diarylethene derivatives.[6] Molecular switches based on bimolecular photochromic systems have received far less attention, despite them offering the distinct advantage of being able to bring together two molecules in a reversible fashion. Thus, for example, the [4 + 4] cycloaddition of anthracene has been used in the assembly[7] and cross-linking[8] of polymers, in the creation of dynamic receptors,[9] and as a means of attenuating magnetic interactions.[10,11]

Unfortunately, these photocycloaddition reactions suffer from poor specificity. For example, irradiation of a mixture of two anthracene derivatives A and B generally leads not only to the AB product, but also to the homodimers AA and BB.[12] This tendency to form complex mixtures severely restricts the usefulness of existing bimolecular photochromic systems. For example, recent attempts to create reversible diblock copolymers from anthracene-terminated segments were hampered by the accompanying formation of the unwanted AA and BB photoproducts.[13] Identifying pairs of chromophores that exclusively form AB cross-dimers would therefore greatly extend the range of materials that could be reliably and reversibly assembled using light. To this end, we have set out to design pairs of complementary anthracene derivatives that selectively form cross-dimers rather than homodimers.[14]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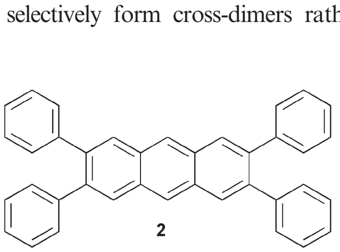
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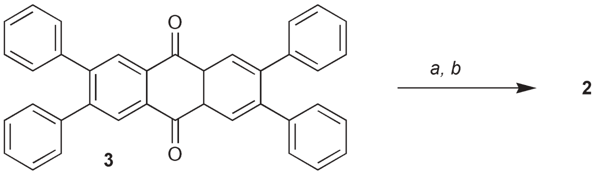
Sterically-hindered anthracene derivatives, such as 9,10-dimethylanthracene (**1**), exhibit only a limited tendency to homodimerize.[15] However, this compound reacts quite readily with anthracene derivatives that lack functional groups at the 9- and/or 10-positions.[12] Unfortunately, since anthracene and its 9-substituted derivatives tend to form homodimers, the reactions involving these compounds still exhibit poor specificity.[16] In an effort to design a suitable partner for **1**, we decided to target an anthracene derivative that lacked groups at the 9- and 10-positions, but substituted bulky groups at the peripheral 2-, 3-, 6- and 7-positions. It was reasoned that a substitution pattern of this type would inhibit homodimer formation while permitting reaction with 9,10-disubsituted derivatives such as **1**. A similar strategy has been successfully employed to attenuate the deleterious effects of self-association on the photophysical properties of conjugated polymers while still allowing interactions with small molecule analytes.[17] Since phenyl groups have been used extensively as "insulation" for both reactive functionalities[18,19] and nanostructured materials,[20–23] it was thought that 2,3,6,7-tetraphenylanthracene (**2**) would possess sufficient lateral bulk to inhibit homodimerization.

Compound **2** was synthesized by $LiAlH_4$–$AlCl_3$ reduction[24] of the corresponding tetraphenylanthraquinone **3**, which itself was recently synthesized in our laboratory from 3,4-diphenylthiophene.[25] The conversion of **3** to **2** under these conditions was accompanied by the formation of an approximately equimolar quantity of the over-reduced product 2,3,6,7-tetraphenyl-9,10-dihydroanthracene. We found that this impurity could be cleanly rearomatized to **2** by treating it with oxygen in the presence of catalytic palladium.[26] Rather than separating the products of the $LiAlH_4$–$AlCl_3$ reduction, the crude product mixture was simply heated in the presence of 10% Pd–C under aerobic conditions to afford **2** as the major product (Scheme 1). This extra step not only improved the overall yield of **2**, but also obviated the need to separate it from the over-reduced dihydroanthracene.

In order to investigate the photochemical behavior of this compound, a benzene solution containing 4 mmol of **2** was exposed to near-UV light.[27] Gratifyingly, no reaction was observed, even after 140 min irradiation. This compound



**Scheme 1** Reagents and conditions: (a) 10 equiv. $LiAlH_4$, 4 equiv. $AlCl_3$, THF, reflux 21 h; (b) 10% Pd–C, mixed xylenes, reflux 5 d.

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† Electronic Supplementary Information (ESI) available: Full synthetic and analytical details of **2** and **4**; $^1H$ NMR spectra of **4** before and after heating at 150 °C; absorption spectra of compounds **1**, **2** and **4**. See http://www.rsc.org/suppdata/cc/b5/b502183a/

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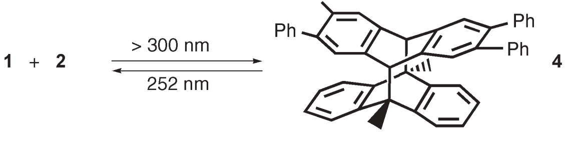
was also photochemically unreactive in acetonitrile, indicating that its failure to dimerize can be traced to the effectiveness of its phenyl groups at inhibiting self-association rather than an effect relating to solvent polarity.[12] Similarly, compound **1** did not react under these conditions, whereas anthracene was converted to dianthracene in 78% yield.

Although compounds **1** and **2** failed to react in isolation, irradiation of an equimolar mixture of them for 140 min under the same conditions afforded a single product in 65% yield (Scheme 2). This product showed a high degree of thermal stability and could be isolated from the starting materials by either column chromatography or recrystallization.

Both the $^{1}$H and $^{13}$C NMR spectra of this photoproduct are consistent with cross-dimer **4**. Of particular note is the presence of two singlets in the $^{1}$H NMR spectrum at 4.1 and 2.2 ppm, corresponding to the dimer's bridgehead protons and methyl groups respectively. These chemical shifts are almost identical to those of the head-to-tail dimer of 9-methylanthracene,[28] as one would expect given their similar chemical environments (*i.e.* a bridgehead proton adjacent to a methyl group). This assignment was further confirmed by the observation of a strong nuclear Overhauser effect between these two sets of protons, indicating that they are in close proximity to each another. Characterization of this compound by mass spectrometry posed a greater challenge, since dianthracenes tend to fragment into their component monomers when ionized.[29] Thus, the MALDI–TOF spectrum of **4** exhibited only peaks corresponding to the two monomers, while the FAB spectrum showed a weak molecular ion peak for the dimer, in addition to a much more intense peak for compound **2**.

Having demonstrated that **1** and **2** selectively form the cross-dimer, we next examined the reversibility of this reaction—since anthracene dimers are known to revert either thermally or photochemically to their component monomers.[29] As is typical for dianthracenes, the UV–visible absorption spectrum of compound **4** is blue-shifted relative to both monomers **1** and **2**, with a $\lambda_{\max}$ of 259 nm. Exposing a sample of **4** to 252 nm light[30] caused the characteristic anthracene peaks of **1** and **2** to appear in the UV–visible spectrum. These peaks became progressively more intense with longer exposure times (Fig. 1), and photoreversion was 56% complete after 90 min.

Compound **4** was found to possess considerable thermal stability at room temperature; indeed, no decomposition of it was observed at temperatures below 100 °C. The thermal reversion of this compound was more thoroughly investigated by $^{1}$H NMR (Fig. S2†). After heating a sample of **4** in DMSO-$d_6$ at 135 °C for 15.5 h, only 15% of the dimer had been converted to monomers **1** and **2**. At 150 °C, approximately 50% of **4** had been consumed after 70 min. The reaction was approximately 93% complete after 150 min at the same temperature. This rate of fragmentation is similar to that of the head-to-tail dimer of 9-methylanthracene,[28] which also has two methyl groups at the bridgehead positions. This suggests that it is the number of bridgehead methyl groups that limits the thermal stability, and that the peripheral phenyl groups do not appreciably destabilize the photodimer. The slow decomposition of this compound at low temperatures indicates that dimers of this type could be used to construct relatively robust structures.



**Scheme 2** The reversible formation of **4** from **1** and **2**.

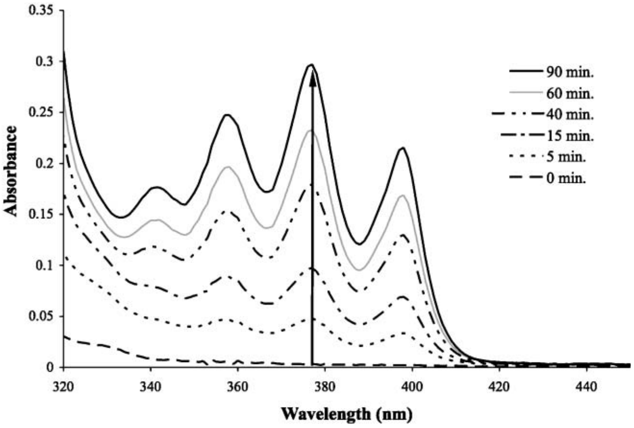


**Fig. 1** The UV–visible absorption spectra after 0, 5, 15, 40, 60 and 90 min of a 0.04 mM solution of **4** in $CH_3CN$ irradiated with 252 nm light.

In conclusion, we have demonstrated the viability of a new strategy for enforcing cross-dimer formation in [4 + 4] photocycloaddition reactions by a judicious choice of substituents on the two anthracene derivatives. The resulting photoproduct is thermally stable at moderate temperatures and can be reconverted to its constituent monomers either photochemically or at elevated temperatures. We are currently investigating the scope and limitations of this strategy for enforcing selective cross-dimerization, as well as examining its potential for controlling the reversible, light driven assembly of materials.

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15 Although 9,10-dimethylanthracene has been reported to homodimerize, it does so only under much more stringent conditions than were employed in the present study, and at no time did we observe the formation of this photoproduct. See: H. Bouas-Laurent and A. Castellan, *Chem. Commun.*, 1970, **23**, 1648–1649.
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