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Regio- and stereo-selective [4+4] photodimerization of angular-shaped dialkyltetracenedithiophene†

Tze-Gang Hsu,^a Hsiao-Chieh Chou,^a Ming-Ju Liang,^a Yu-Ying Lai^b *^b and Yen-Ju Cheng^{*}

Angular-shaped dialkyltetracenedithiophenes (aTDTs) undergo [4+4] photodimerization in solution to form a butterfly-shaped skeleton. This reaction proceeds in a regio- and stereo-selective manner, forming only a single planosymmetric *syn*-[2,2]-daTDT out of six possible products. The photocycloaddition of aTDTs can take place topochemically in the thin-film state while maintaining regio- and stereo-selectivity. Stronger aliphatic dispersion forces and $\pi-\pi$ interactions play important roles in forming the eclipsed dimeric complex that leads to the *syn*-[2,2]-daTDT isomer.

Acenes, polycyclic aromatic hydrocarbons (PAHs) comprising linearly fused benzene rings, have exhibited great potential as organic semiconductors.¹ Tetracene and pentacene derivatives are especially of current interest due to their superior hole mobility due to the enhancement of π - π stacking in the solid state.² Increasing the number of benzene rings in acenes simultaneously results in a narrower optical bandgap and thus higher photo-reactivity.^{1b,3} Highly planar acene derivatives undergo visible-light induced [4+4] cycloaddition to furnish 3-dimensional dimers with unique butterfly-shaped skeletons. The light-triggered dimeric formation with concomitant disruption of the π -conjugation significantly alters the optical absorption and emission wavelengths. The dramatic change in the steric and electronic properties between acene and the photodimer has attracted much research interest to experimentally or theoretically investigate the reaction mechanism.2f,4 The most problematic drawback of this chemistry is that photodimerization of an acene inevitably yields a mixture of geometric isomers due to the fact that multiple reactive benzene moieties embedded in an acene

(tetracene, pentacene or larger acenes) are able to participate in cycloaddition. Some photodimers from a single acene cannot be easily purified and characterized. In addition, it is difficult to obtain single crystals of the dimeric molecules suitable for decisive X-ray diffraction analysis.^{4d,5}

The unpredictable or unidentified structures of the photodimers greatly hinder the photochromic applications of acene derivatives.⁶ For example, photoinduced-dimerization of unsubstituted tetracene forms centrosymmetric (head-to-tail) and planosymmetric (head-to-head) dimers (Scheme 1). The centrosymmetric photodimer is found to be the major product^{4f,7} due to the smaller steric hindrance and repulsion of the π -electron system of the bimolecular sandwich-like alignment during the transition state.^{4b,c,f} When tetracene is further substituted with solubilizing groups, more geometric arrangements of two interacting monomers are possible in the transition state, leading to the formation of more complicated isomeric products.^{4d,7c} For instance, photodimerization of 2,3-didecyloxytetracene leads to the formation of four different regio- and stereo-isomers in a similar ratio.⁵ Therefore, controlling the selectivities of acenebased [4+4] photo-cycloadditions remains challenging and unsolved.

So far only scarce tetracene derivatives have been prepared on account of their poor solubility, instability, and lack of a



Scheme 1 (a) Planosymmetric (left) and centrosymmetric (right) photodimers of tetracene (b) photodimerization of 2,3-didecyloxytetracene and (c) photodimerization of angular tetracenedithiophene (aTDT) in this work.

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^a Department of Applied Chemistry, National Chiao Tung University, 1001 University Road, Hsinchu, Taiwan 300, Republic of China.

E-mail: yjcheng@mail.nctu.edu.tw

^b Institute of Polymer Science and Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Rd, Taipei 10617, Taiwan, Republic of China. E-mail: yuyinglai@ntu.edu.tw

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versatile synthetic methodology, which limits further investigation. It is of substantial interest to develop a new tetracene-based system which favors selectively a butterfly-shaped photodimer and allows for fundamental understanding of structure-selectivity relationships. To this end, terminally fusing a tetracene with two thiophenes to afford tetracenedithiophene (TDT) is a rational design to enhance π - π interactions and improve molecular stability.8 It is documented that angular-shaped acenedithiophenes possess lower-lying HOMO levels than the corresponding linear-shaped one,⁹ resulting in a better ambient stability, which is advantageous to handle and examine the [4+4] photodimerization product.¹⁰ Herein, we have successfully developed a new methodology to synthesize an angular tetracenedithiophene (aTDT) derivative with two lateral aliphatic side chains at the 4 and 11 positions to impart solubility. The aTDT is thermally stable but undergoes dimerization upon illumination with visible light (420-460 nm). Six possible photodimers (daTDT) including two enantiomers (syn-[2,2]-daTDT, syn-[2,3]-daTDT, anti-[2,2]-daTDT and its enantiomer anti-[2,2]'-daTDT, and anti-[2,3]-daTDT and its enantiomer anti-[2,3]'-daTDT) are theoretically anticipated (Chart 1). daTDT is the abbreviation of dimeric aTDT. syn stands for the two up and down thiophenes aligning syn to each other and anti represents an anti-configuration. 2 and 3 denote that the bridge carbon lies on the second and third benzene ring of the central tetracene core numbered from the left, respectively. Surprisingly, this reaction exclusively affords the planosymmetric syn-[2,2]-daTDT. To the best of our knowledge, this is the first time that photodimerization of an acene derivative forms a planosymmetric dimer with such a high regioand stereo-selectivity.

Synthesis of aTDT1 with decanyl side chains is described in Scheme 2. Stille coupling of **1** with tributyl(2-thienyl)stannane furnished 2. Subsequently, Sonogashira cross-coupling reaction of **2** with 1-dodecyne afforded **3a**. PtCl₂-catalyzed 6-electrocyclization of **3a** led to the formation of the central tetracene core of aTDT1 with two side chains at the 4 and 11-positions. The structure of aTDT1 was unambiguously confirmed by single-crystal X-ray crystallography. To investigate the side-chain steric effect, aTDT2 with branched 2-octyldodecyl groups was also prepared for comparison.

When a CDCl₃ solution of aTDT1 was illuminated by visible light (420–460 nm), aTDT1 gradually converted into a new

Chart 1 Six possible stereoisomers and corresponding symmetry point groups for daTDT, in which *anti*-[2,2]-daTDT/*anti*-[2,2]'-daTDT and *anti*-[2,3]-daTDT/*anti*-[2,3]'-daTDT are enantiomers.

anti-[2,3]-daTDT, C2

syn-[2.3]-daTDT, Ci

2]-daTDT, C2

anti-[2,3]'-daTDT, C2



Scheme 2 Synthetic route of aTDT1 and aTDT2



Fig. 1 Time-dependent UV-Vis spectra of aTDT1 under light illumination (420–460 nm); inset: the green emission is bleached after irradiation.

photodimer whose UV-Vis spectra and ¹H NMR spectra are presented in Fig. 1 and 2, respectively. The absorption intensity of aTDT1 from 350 to 500 nm gradually diminished as a function of irradiation time, implying the formation of the butterfly-skeleton dimer via photo-induced [4+4] cycloaddition with disconnection of the original conjugation (Fig. 1). In addition, the dimerization is reversible when syn-[2,2]-daTDT1 is stored in the dark without interruption. Although not fully reverted, the reversibility of syn-[2,2]-daTDT1 is clearly observed after months (Fig. S1, ESI⁺). This newly-formed compound is highly viscous and the attempt at recrystallization of this compound was not successful owing to its high solubility even in apolar organic solvents. Judging from the ¹H NMR spectra monitored as a function of irradiation time (Fig. 2), it can be concluded that only a single photodimer out of the six possible isomers was gradually formed during the reaction. The chemical



Fig. 2 Time-dependent ¹H NMR spectra of photo-dimerization of aTDT1 (420–460 nm) and labels for syn-[2,2]-daTDT1 (see Chart 1).

vn-[2.2]-daTDT. Cs

anti-[2,2]'-daTDT, C2

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shifts at 6.29 and 6.43 ppm in Fig. 2 are assigned to the typical hydrogens on the sp³-bridgehead carbon of the butterfly-dimer.^{4d,5} The neighboring two bridgehead protons in *syn*-[2,3]-daTDT1 and *anti*-[2,2]-daTDT1 should couple with each other to exhibit two doublets, because they are chemically nonequivalent. On the other hand, the bridge head hydrogens on *syn*-[2,2]-daTDT1 and *anti*-[2,3]-daTDT1 are chemically equivalent and expected to exhibit two singlets. The observation of two singlet peaks instead of doublet peaks explicitly rules out the possibility of *syn*-[2,2]-daTDT1 and *anti*-[2,2]-daTDT1. In other words, only *syn*-[2,2]-daTDT1 or *anti*-[2,3]-daTDT1 could possibly be the product.

With the help of heteronuclear single quantum coherence spectroscopy (HSQC) and heteronuclear multiple bond correlation spectroscopy (HMBC), the individual carbons and hydrogens of daTDT1 can be assigned accordingly (Fig. S2–S7, ESI†). The numbering of the side chains for the hindsight structure is shown in Fig. 3. We define α , β , and "internal" for the first, second, and internal carbons on the decanyl group respectively. "L" denotes the left-sided decanyl group attached to the benzothiophene moiety while "R" signifies the right-sided decanyl group linking to the naphthothiophene segment and prime is used to distinguish the upper and lower moieties. Nevertheless, the combination of HSQC and HMBC spectroscopy is not sufficient to elucidate the exact stereochemistry of daTDT1. ROESY (rotating-frame nuclear Overhauser effect correlation spectroscopy) was then employed to further characterize daTDT1 (Fig. 4).

In the resultant spectrum, signal A corresponds to the coupling between hydrogens on the right-sided first $(H_{\alpha R})$ and



Fig. 3 Labels of the side chain hydrogens for syn-[2,2]-daTDT1.



Fig. 4 ROESY spectrum of syn-[2,2]-daTDT1 in a selected range.

second $(H_{\beta R})$ carbons. In the same way, B is the coupling between $H_{\alpha L}$ and $H_{\beta L}.$ Searching along the horizontal dotted line of B, signals C $(H_{\alpha L}-H_{internal}')$ and D $(H_{\alpha L}-H_{internal}')$ are perceived. These signals, based on the HSQC and HMBC interpretation, are characterized to be the correlations of $H_{\alpha L}$ - $H_{internal}$ or $H_{\alpha L}$ - $H_{internal}'$. However, the analogous $H_{\alpha R}$ - $H_{internal}$ or $H_{\alpha R}$ - $H_{internal}'$ coupling on the naphthothiophene side of daTDT1 is not yet detected. It should be emphasized that neither $H_{\alpha L}$ - $H_{internal}$ nor $H_{\alpha R}$ - $H_{internal}$ coupling is observed in the ROESY NMR spectrum of the aTDT1 monomer (Fig. S8, ESI⁺). The exclusive detection of $H_{\alpha L}$ - $H_{internal}$ couplings in daTDT1 strongly indicates that the top and bottom decanyl moieties attached to the benzothiophene segments are in close proximity, which is only possible for syn-[2,2]-daTDT1 with the two decanyl groups situated on the same side.¹¹ Another probable photodimer, anti-[2,3]-daTDT1, with the upper and lower side chains pointing in different directions is reasonably ruled out. syn-[2,2]-daTDT1 can be concluded as the product of the photoinduced dimerization. The chemical shift of each proton in syn-[2,2]-daTDT1 is assigned in Fig. 2 after 45 min irradiation. To further discuss the ROESY $H_{\alpha}L-H_{internal}$ signals in Fig. 4, the encounter of the aliphatic side chains induces inter-chain nuclear Overhauser effect (NOE) enhancement. On the other hand, the absence of a long-range NOE signal for the naphthothiophene parts suggests that the upper and lower decanyl groups in the naphthothiophene sides are too far away in comparison to the benzothiophene side.

The formation of *syn*-[2,2]-daTDT1 from two aTDT1 molecules is not only regioselective but also stereoselective. The X-ray crystallography of aTDT1 is shown in Fig. 5 to illustrate the dimeric packing extracted from the extended stacks in the crystal structure. It is found that the two aTDT1 molecules align in a *syn* manner rather than an *anti* one, which may be linked to the presence of two lateral decanyl groups. The dispersion forces induced by the aliphatic side chains might play a significant role in aligning the eclipsed face-to-face dimeric complex leading to the preferable *syn*-[2,2]-daTDT isomer. Moreover, the emission spectra for aTDT1 are listed in Fig. S10 (ESI†). The increase in concentration from 1.04×10^{-3} M to 5.24×10^{-3} M gives rise to the emergence of a new emission band at lower energies, suggesting the formation of aTDT excimer.

To investigate the general photo-selectivity of the aTDT system, we synthesized aTDT2 with branched 2-octyldodecyl



Fig. 5 Extracted dimeric packing of aTDT1 in the single crystal structure of X-ray crystallography: (a) top view and (b) side view.

side chains that impose larger steric hindrance during dimerization. The NMR analyses again demonstrate that syn-[2,2]-daTDT2 is still the single photodimer with identical regioselectivity and stereoselectivity in solution. It is of great interest to further investigate the photodimerization in the solid state. The X-ray diffraction (XRD) patterns of aTDT1 powder and single crystal are compared in Fig. S11 (ESI⁺). The close resemblance between the two patterns suggests that the powder sample possesses a similar solid-state stacking structure to the single crystal shown in Fig. 5. Upon direct exposure to irradiation, the aTDT1 powder remain unreacted. Solvent vapour annealing of the aTDT1 powder was therefore attempted. When aTDT1 is saturated with *d*-chloroform vapour in a closed jar under 420-460 nm irradiation, photodimerization proceeds gradually to form a single isomer which is also determined to be syn-[2,2]-daTDT1. d-Chloroform vapour would penetrate into the powder to slightly dissolve the aTDT1 molecules, rendering them with sufficient freedom for structural transformation. It is envisaged that the two aTDT1 molecules in the syn geometry undergo molecular slippage from the offset face-to-face stacking to the eclipsed face-to-face stacking before dimerization, leading to the syn-[2,2]-daTDT1 product. In addition to the aliphatic dispersion interactions, it is also envisaged that the eclipsed fact-to-face dimeric stacking would have stronger π - π interactions than the offset fact-to-face stacking. The thermodynamically more stable eclipsed complex might account for the selectivity of syn-[2,2]-daTDT over syn-[2,3]-daTDT.

Furthermore, an aTDT2 thin film was prepared by spincoating of its solution on a glass slide. After 15 min light irradiation, the original yellow thin film became totally transparent, demonstrating that photodimerization can successfully take place in the thin-film state (Fig. S12, ESI⁺). More importantly, the product was collected and proven to be the syn-[2,2]-daTDT2 as the single product again. Compared with the XRD of aTDT2 powder, the aTDT2 thin film exhibits more diverse XRD peaks (Fig. S13, ESI[†]), suggesting that the aTDT2 thin film should be polymorphic. Considering that the photodimerization of the anthracene single crystal actually occurs in its defects,¹² the polymorphic packing in the aTDT2 thin film might be responsible for the distinct photo-reactivity. To our knowledge, this study is the first demonstration that a tetracene-based material can carry out a light-induced topochemical reaction with high regio- and stereo-selectivity.

In summary, we have developed dialkyl angular-shaped TDTs (aTDT1 and aTDT2) which undergo [4+4] photodimerization reaction to form a butterfly-shaped *syn*-[2,2]-daTDT. Instead of the sterically-favored centrosymmetric *anti*-[2,3]-daTDT, the plano-symmetric *syn*-[2,2]-daTDT surprisingly turns out to be the single isomer out of six possible products. The structure of *syn*-[2,2]-daTDT is carefully determined by a series of NMR techniques including ¹H, ¹³C, HSQC, HMBC, and ROESY, as well as mass spectrometry. Side-chain interactions inducing self-assembly may dictate the regio- and stereo-selectivity. Most importantly, the photodimerization can take place topochemically in the thinfilm state as well as in the solvent-annealed powder while maintaining its original regio- and stereo-selectivity. The in-depth understanding of the photodimerization in the aTDT

system provides guidelines to design smart acene-based materials which are promising for photochromic and photo-responsive applications.

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Conflicts of interest

There are no conflicts to declare.

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