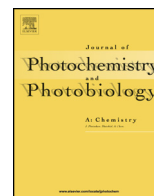




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Critical control by scaffold flexibility achieved in diastereodifferentiating photocyclodimerization of 2-anthracenecarboxylate

Gaku Fukuhara*, Kazuhiro Iida, Tadashi Mori, Yoshihisa Inoue

Department of Applied Chemistry, Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan

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This paper is dedicated to Professor Yoshihisa Inoue on the occasion of his retirement from Osaka University.

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ABSTRACT

By progressively increasing the flexibility of chiral vicinal diol scaffold (from rigid cyclic tetrasaccharide to flexible 2,3-butanediol via glucose and *trans*-1,2-cyclohexandiol) in the diastereodifferentiating photocyclodimerization to *head-to-head* (HH) dimers of 2-anthracenecarboxylate on the scaffold, the *anti/syn* preference was dramatically inverted from 42:1 to 1:12, while the enantiomeric excess of the chiral *anti*-HH dimer was consistently kept high at >99% due to the excited-state dynamics that strongly disfavors the *si-si* enantiotopic face attack against the antipodal *re-re* face attack, exclusively affording the (*P*)-enantiomer.

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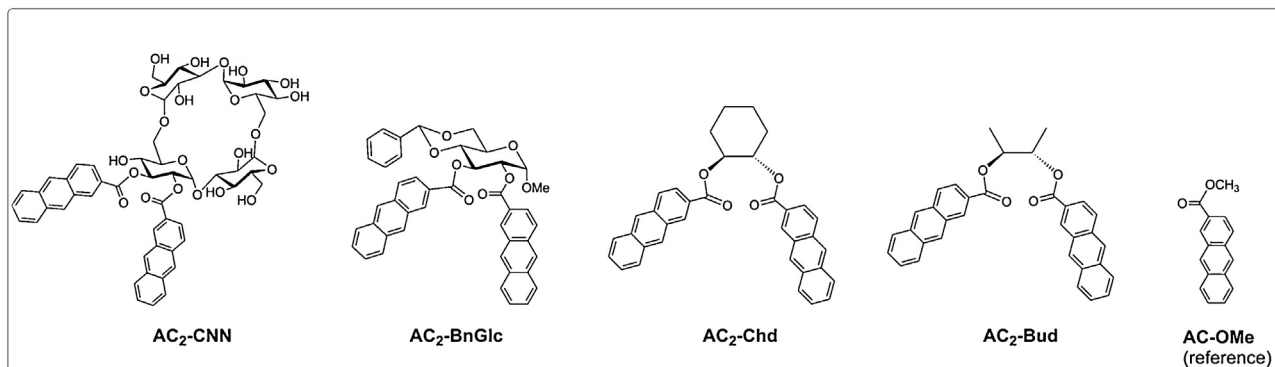
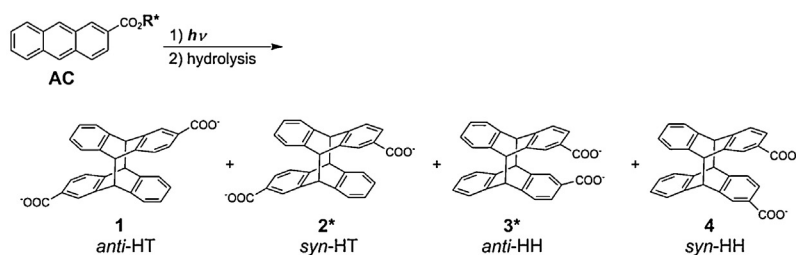
1. Introduction

Photochirogenesis with high chemical and optical yields has not been an easy goal to achieve for photo- and synthetic chemists [1]. Thus, the high diastereomeric excesses (de's) reported for various photochirogenic reactions exploiting chiral auxiliaries and scaffolds have often been achieved in modest chemical yields, which would have rendered the photochirogenic routes less attractive than the thermal asymmetric syntheses with chiral catalysts and enzymes [2]. Indeed, a variety of diastereodifferentiating photoreactions have been reported with good-high de's since mid-1970s, as exemplified by the photocyclization of diarylethenes (28–100% de) [3], the photoisomerization of cyclooctene (21–43% de) [4], [2 + 2] the photocyclodimerization of cinnamates (46–97% de) [5], the photocycloaddition of enones to olefins (56–91% de) [6], and the Paternò–Büchi reaction of ketones with olefins (7–97% de) [7], but high chemical yields have rarely been achieved simultaneously.

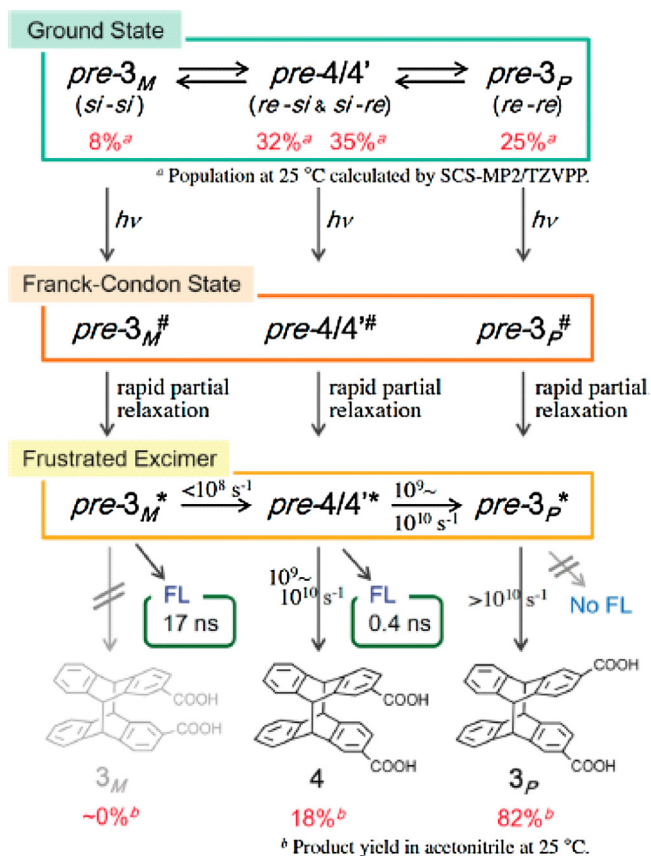
We have investigated the diastereodifferentiating [4 + 4] photocyclodimerization of 2-anthracenecarboxylate (AC) tethered to cyclic nigerosyl nigerose (CNN) [8] and also to methyl 4,6-*O*-benzylidene- α -D-gluopyranoside (BnGlc) [9] (Scheme 1). Both of the scaffolded substrates, i.e. **AC**₂-CNN and **AC**₂-BnGlc, have achieved the ultimate goal of simultaneously obtaining high optical and chemical yields by almost exclusively affording the (*P*)-enantiomer of *anti-head-to-head* (*anti*-HH) cyclodimer (**3_P**) [10] in >99% enantiomeric excess (ee) and 96% yield after removal of the saccharide scaffold. The mechanistic details of the latter reaction have recently been elucidated by combined theoretical conformational analyses and experimental circular dichroism (CD) spectral and photophysical studies [9]. In this photochirogenic reaction, the product distribution, determining the yield and ee, is controlled not by the ground-state thermodynamics but by the excited-state dynamics, as illustrated in Scheme 2 [9]. In the ground state, **AC**₂-BnGlc populates over the energetically closely lying four conformers, i.e. *pre*-**3_P** (25% population), *pre*-**3_M** (8%), *pre*-**4** (32%), and *pre*-**4'** (35%), which are the precursors to **3_P** (formed via the *re-re* attack, where the two ACs on the scaffold cyclodimerize from the confronting *re* and *re* enantiotopic faces), **3_M** (*si-si*), **4** (*re-si*), and again **4** (*si-re*), respectively. Upon excitation, these four conformers are promoted to the corresponding Franck–Condon

* Corresponding author.

E-mail address: gaku@chem.eng.osaka-u.ac.jp (G. Fukuhara).



Scheme 1. Diastereodifferentiating photocyclodimerization of 2-anthracenecarboxylate (AC) tethered to chiral scaffolds (R^*).



Scheme 2. Mechanism of the diastereodifferentiating photocyclodimerization of AC_2 -BnGlc controlled by the dynamics of frustrated excimers. Reprinted with permission from G. Fukuhara, K. Iida, Y. Kawanami, H. Tanaka, T. Mori, Y. Inoue, J. Am. Chem. Soc. 137 (2015) 15007–15014. Copyright 2015 American Chemical Society.

states $pre-3_P^{\#}$, $pre-3_M^{\#}$, $pre-4^{\#}$, and $pre-4'^{\#}$, which partially relax to “frustrated excimers” $pre-3_P^*$, $pre-3_M^*$, $pre-4^*$, and $pre-4'^*$ due to the steric restrictions of the BnGlc scaffold. If the product ratio is determined solely by the ground-state thermodynamics, this population should give **3** in 33% yield and –52% ee, which however distinctly differed from the experimental values of 82% yield and >99% ee. This is because $pre-3_M^*$ cannot cyclodimerize due to the strain and hence fluoresces or isomerizes on the excited-state potential surface to $pre-4/4'^*$ and then to $pre-3_P^*$, the latter of which spontaneously cyclodimerizes to **3_P**. These results enabled us to conclude that the dynamic excited-state conformer equilibrium and the subsequent cyclodimerization kinetics overwhelm the conformer population determined thermodynamically in the ground state [9], and certainly expanded the scope of photochirogenesis, but the limitations have not clearly been explicated.

In the present study, we wanted to elucidate how and to what extent the excited-state dynamics can manipulate the stereochemical fates of the diastereodifferentiating photocyclodimerization of AC by performing the photoreactions on more flexible chiral scaffolds, i.e. cyclic *trans*-1,2-cyclohexanediol (Chd) and acyclic 2,3-butanediol (Bud) (Scheme 1), and comparing the results with those obtained for more rigid CNN and BnGlc scaffolds [8,9]. The comparison will reveal the scope and limitations of the excited-state dynamics control strategy as a general tool for simultaneously achieving high chemical and optical yields in scaffold-based diastereodifferentiating photoreactions.

2. Experimental

2.1. Instruments

1H NMR spectra were recorded at 400 MHz in $CDCl_3$ on a JEOL GX-400 instrument. UV/vis and CD spectra were measured in a quartz cell ($10 \times 10 \times 45$ mm) on JASCO V-650 or V-560 and J-720WI or J-820YH spectrometers, respectively, both equipped with an ETC-505T temperature controller. Fluorescence spectra were recorded on a JASCO FP-6500 spectrofluorimeter. Fluorescence lifetimes were determined by Hamamatsu Quantaaurus-Tau

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