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X-ray observations of single bio-supramolecular photochirogenesis

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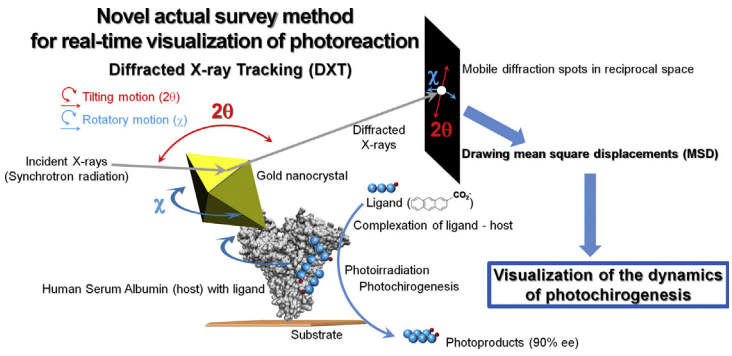
GRAPHICAL ABSTRACT



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ABSTRACT

The binding and photochirogenic behaviour of 2-anthracenecarboxylate (AC) with human serum albumin (HSA) have hitherto been investigated and comprehended as time-averaged statistical events by spectroscopic examinations and product analyses. In this study, we employed a diffracted X-ray tracking (DXT) technique to visualize the single-molecular dynamics of free and AC-loaded HSA (AC:HSA = 0, 1, 5 and 10), as well as the AC-HSA complex under photoirradiation, all of which were tethered to gold nanocrystals and hence traceable in real time by DXT. This enabled us to draw a more dynamic picture of the bio-supramolecular photochirogenesis at a single-molecule resolution, detailing the softening and flexibility enhancement of HSA upon binding of ACs to its inter-subdomain IIA-IIB site and the dynamic extrusion of AC dimers produced upon photoirradiation.

1. Introduction

Human serum albumin (HSA) is the most abundant protein in human plasma and functions as a transporter/reservoir of various endogenous and exogenous hydrophobic molecules such as fatty acids, bilirubins, hormones, and many pharmaceuticals in its ligand-specific binding sites [1–10]. These hydrophobic binding sites are three-dimensional, well organized, and inherently chiral. We have employed

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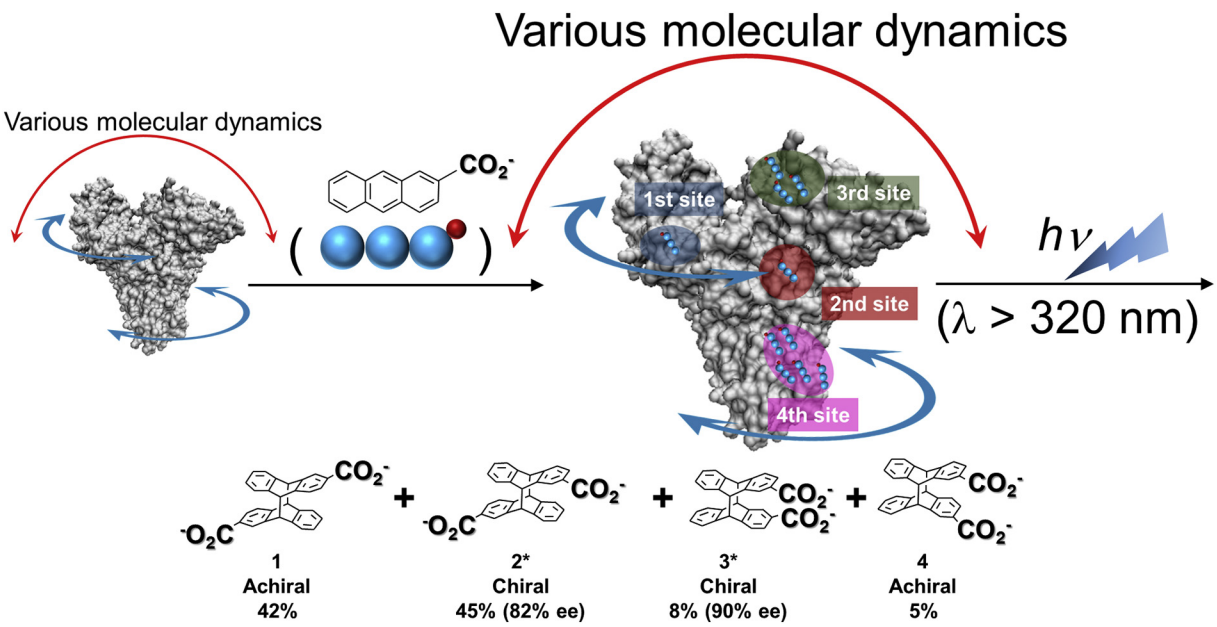

Fig. 1. Bio-supramolecular photochirogenesis of 2-anthracenecarboxylate in the first to fourth binding sites of HSA, accepting achiral cyclodimers 1 and 4 and chiral cyclodimers 2 and 3 in high enantiomeric excesses.

these binding pockets as a chiral environment for affecting the enantiodifferentiating photocyclodimerization of 2-anthracenecarboxylate (AC) to obtain a mixture of four stereoisomeric cyclodimers 1–4 (Fig. 1), two of which are chiral and obtained in higher enantiomeric excesses of up to 90% upon irradiation with HSA than other photocatalysts [11–14]. We have elucidated the AC binding sites and stoichiometries as well as their photochirogenic performance in a series of spectroscopic and photochemical studies [15–18]. Nevertheless, we still know little about the events occurring inside HSA upon AC complexation and the supramolecular consequences of AC-HSA complex photoirradiation, which hinders our molecular-level understanding of the dynamic complexation and photochirogenesis processes.

In this study, we visualize the binding and photochirogenic behaviour of HSA with and without AC molecules bound to its first to fourth binding sites at a single-molecule level using the real-time monitoring of the Brownian motion of AC-HSA complexes (AC/HSA = 0, 1, 5, and 10) with a diffracted X-ray tracking (DXT) method (Fig. 2) [19–27]. DXT is a state-of-the-art technique invented by one of the present authors for tracking the Brownian motion of a single target molecule with high angular accuracy (< 0.05°), while avoiding any significant physical or chemical perturbations, which is enabled by chasing the X-ray spots diffracted from a gold nanocrystal (< 100 nm) attached to the target (< 10 nm) of a comparable or larger size. Although it shall be assigned using the real size effect of this HSA, the target host molecule in DXT is known, as the size of gold nanocrystal has little effect on the dynamics of the target molecules. For a molecular-level understanding of HSA-mediated bio-supramolecular photochirogenesis, DXT is expected to allow us to directly observe the dynamic behaviour of a gold nanocrystal-tagged single HSA molecule before and after the binding of different equivalents of AC as well as the effects of photoirradiating the AC-HSA complex track on *in-situ* Brownian motion in real time. Combining the dynamic physical inspection *via* the static (photo)chemical investigation, we can draw a more precise dynamic picture of this highly efficient, but dynamically less elucidated bio-supramolecular photochirogenesis. (See Fig. 3.)

2. DXT of HSA and AC-HSA complexes

Conventionally, gold nanocrystals are tethered to a single biomolecule anchored to an amorphous gold substrate with a long-chain N-

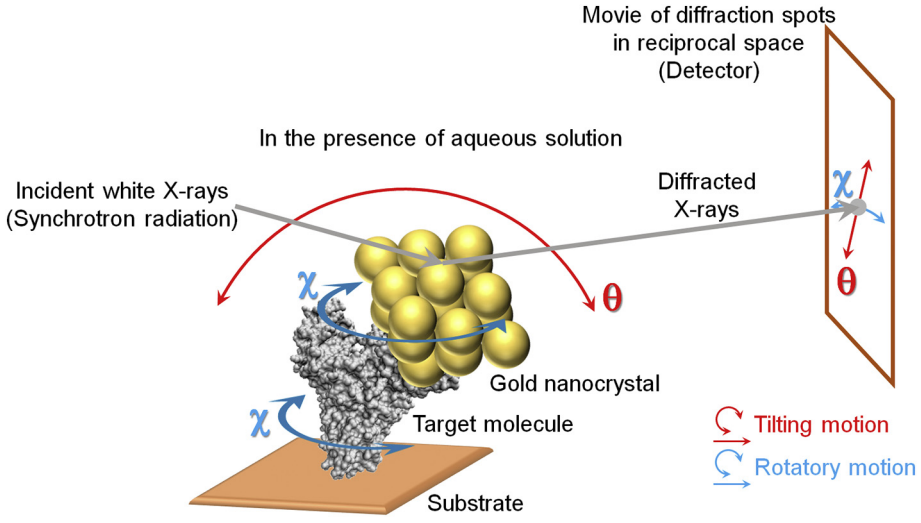

Fig. 2. Schematic illustration of the principle of diffracted X-ray tracking (DXT). The marker is a gold nanocrystal tethered to the target protein on an amorphous gold substrate dipped into a phosphate buffer at pH 7. The movement of the diffraction spots from the gold nanocrystal–caused by the θ- and χ-directional motion of the target molecule–is monitored by a CCD camera and image intensifier, and recorded in real time as a movie at a rate of ≥90 frames s^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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