

Highly Enantioselective Photochromism of C2-Connected Bisthienylethenes in Human Serum Albumin with Long Wavelength UV Light

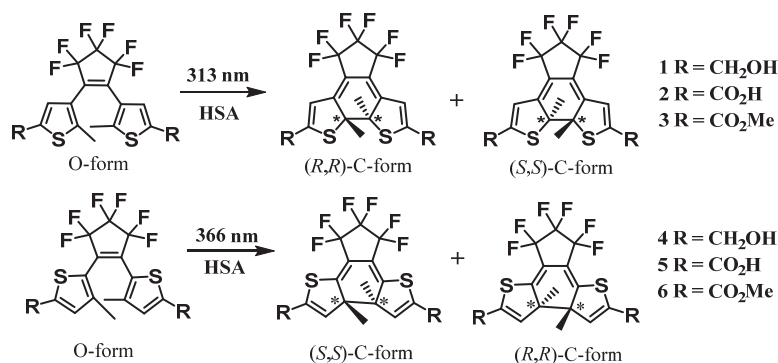
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We have reported the enantioselective photochromic ring closure of bisthienylethenes (BTEs) **1o**, **2o**, **3o** incorporated in Human Serum Albumin (HSA).^{1,2} The BTEs used have the connection of thiophene rings to the ethene bridge at their C3 positions, and the irradiation was carried out with 313 nm UV light. BTEs **2o** and especially **3o** showed highly enantioselective photochromic reactions when the reaction medium was 85% phosphate buffer solution (PBS) and 15% acetonitrile (v/v).²

In the present research we employed BTEs **4o**, **5o**, **6o** with the connections at their C2 (Scheme 1). Since the open forms of these BTEs have absorption maxima in the longer wavelength,³ we can use less harmful 366 nm light for ring closure. BTEs **4o**, **5o**, **6o** cyclized in PBS containing acetonitrile when irradiated with 366 nm light.



Scheme 1. Stereochemistry of closed forms of BTEs

Enantiomer excess (ee) values of BTEs **4c**, **5c**, **6c** were measured by the HPLC equipped with a chiral column. BTE **5o** showed 98% ee when acetonitrile added was 1% when the molar ratio of HSA/BTE was 10, and decreased gradually upon further addition. Ee values of BTEs **4c** and **6c** increased by the addition of acetonitrile until 10% for **4c** (31% ee) and 13% for **6c** (80% ee). These results indicate that addition of acetonitrile (i) disturbed the highly enantioselective fixation of the conformation of **5o** in HSA, (ii) improved the enantioselective fixation of conformation of **4o** and **6o** in HSA largely, and (iii) the ee values are considerably higher for the carboxylic acid derivatives **5o** and **6o** than the alcohol **4o**.

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References:

- [1] M. Fukagawa, I. Kawamura, T. Ubukata, Y. Yokoyama, *Chem. Eur. J.*, **2013**, 19, 9434.
- [2] K. Kawamura, K. Osawa, Y. Watanobe, Y. Saeki, N. Maruyama, Y. Yokoyama, *Chem. Commun.*, **2017**, *in press*, DOI: 10.1039/C6CC10197F.
- [3] K. Uchida, M. Irie, *Chem. Lett.*, **1995**, 969.