

Self-Assembling Behavior and Negative Non-Linear Dependence of Hydrogen-Bonded Tris(phenylisoxazoly)benzene Dimers

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Keywords: Self-Assembly; Chirality; Circular Dichroism

Ureido-pyrimidinone (UPy) motif forms a quadruple hydrogen-bonded dimeric pair with a dimerization association constant of $K_{\text{dim}} > 1.0 \times 10^7 \text{ L mol}^{-1}$.¹⁾ Our group reported that tris(phenylisoxazoly)benzene derivatives with chiral side chains were stacked in a columnar fashion to form one-handed helical supramolecular polymers.²⁾ Here, we report the self-assembly behavior of UPy-appended tris(phenylisoxazoly)benzene (*S*)- and (*R*)-**1** in a mixture of CHCl_3 /methylcyclohexane (MCH) (Figure 1a). When the content of MCH was increased to 60%, a strong CD signal with a dissymmetry factor g_{abs} of 0.027 was observed (Figure 1b). On the other hand, no CD signal was observed in the pure CHCl_3 solutions of (*S*)-**1**.

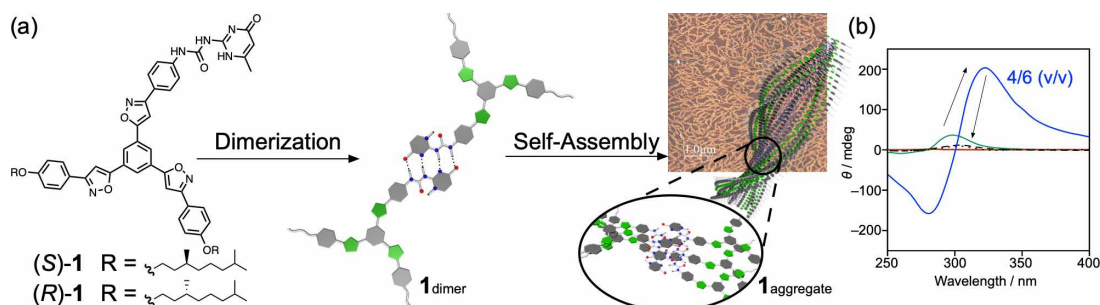


Figure 1. (a) Cartoon representation of the formation of helically twisted supramolecular polymer consisting of **1**. Inserted AFM image was spin-coated film of (*S*)-**1** on mica prepared from its CHCl_3 solution. (b) CD spectra of (*S*)-**1** in CHCl_3 /MCH. The red, black, green, blue, dotted, and broken lines denote the spectra of (*S*)-**1** recorded in CHCl_3 /MCH (v/v) = 10/0, 8/2, 6/4, 4/6, 2/8, and 0/10, respectively. $[(S)\text{-}\mathbf{1}] = 1.0 \times 10^{-4} \text{ mol L}^{-1}$.

The CD spectra were measured when varying the enantiomeric excesses (*ee*) for (*S*)- and (*R*)-**1** mixtures in CHCl_3 /MCH (4/6, v/v). The plot of the net helicity against the *ee* showed negative non-linear dependence at the concentration of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ (Figure 2). We will give a presentation about the detailed discussion on the self-assembly behavior and negative non-linear dependence of (*S*)- and (*R*)-**1** mixtures.

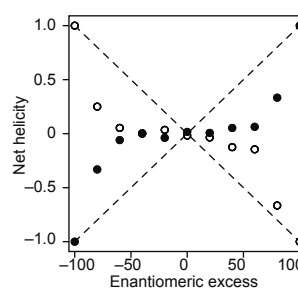


Figure 2. Plot of the net helicity at (closed circle) 280 nm and (open circle) 320 nm against the *ee* of mixed monomer of (*S*)- and (*R*)-**1**.

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