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Electronic Supplementary Information

Time-dependent amplification of helical bias in self-assembled dye nanorods by the sergeants-and-soldiers principle

Andreas Lohr and Frank Würthner*

Universität Würzburg, Institut für Organische Chemie, Am Hubland, D-97074 Würzburg, Germany

E-mail: wuerthner@chemie.uni-wuerzburg.de

1. Experimental

1.1 General aspects

Bis(merocyanine) dyes **1** and (*R*,*R*)-**2** were synthesized according to the previously described procedure.[S1] Solvents for the self-assembly studies were of spectroscopic grade and used as received. Circular dichroism spectra were recorded on a Jasco J-950 spectropolarimeter with a spectral bandwidth of 1 nm, a response time of 0.5 s, and a scan rate of 200 nm/min using a conventional quartz cell (light path 5 mm). The temperature was controlled by a Jasco CDF-426S Peltier element.

1.2 Self-assembly studies

Stock solutions of **1** and (*R*,*R*)-**2** were prepared in tetrahydrofuran (3.33×10^{-5} M) and mixed in different volumetric ratios to obtain monomer stock solutions with fractions of chiral sergeant $\chi_{(R,R)\text{-}\mathbf{2}}$ ranging from 5 to 100%. The aggregation of the monomers into nanorods was accomplished by adding 817 μL of nonpolar methylcyclohexane (MCH) to 350 μL of the THF stock solution of the respective mixtures. These aggregate solutions contain a total monomer concentration of 10^{-5} M in a mixture of THF/MCH = 30:70 (vol%).

As shown previously, for pure (*R*,*R*)-**2**, the monomers aggregate rapidly upon addition of nonpolar MCH owing to the increased Coulomb forces between the dipolar dyes.[S2] At room temperature, the instantaneous dimerization of the chromophores leads to oligomeric species **D**, which self-assemble into **H1** nanorods and subsequently into thermodynamically equilibrated **H2** nanorods (see Fig. S1). These two different types of nanorods show distinct CD spectra and their morphological helical pitch differs significantly as observed by AFM.[S2]

In the present case, we heated the solutions to 47 °C after initiation of aggregation by MCH addition (instead of keeping them at room temperature) to accomplish a quick formation of the **H2** nanorods (Fig. S1). At this elevated temperature, the subsequent "sergeants-and-soldiers" directed chiral amplification process into **H2**-type aggregates with amplified chirality (denoted as **H2'**) still remains slow compared to the initial formation of **H2** aggregates, and can therefore be studied independently in very good approximation. The maxima/minima of the bisignate Cotton effect as well as the isodichroic points observed from the CD spectra during this amplification process are in good accordance with those previously observed for **H2** nanorods formed from pure (*R*,*R*)-**2** monomers,[S2] revealing that the formation of **H2** nanorods is completed prior to the amplification process.

However, a close comparison of the CD spectra of the here studied co-aggregates (Fig. S2) with that of **H2** nanorods formed from pure (*R*,*R*)-**2** reveals a slight hypsochromic shift of the former ones (about 1 nm). Notably, this small difference indicates their co-aggregated nature and can be attributed to a slightly different packing compared with **H2** nanorods from pure (*R*,*R*)-**2**.

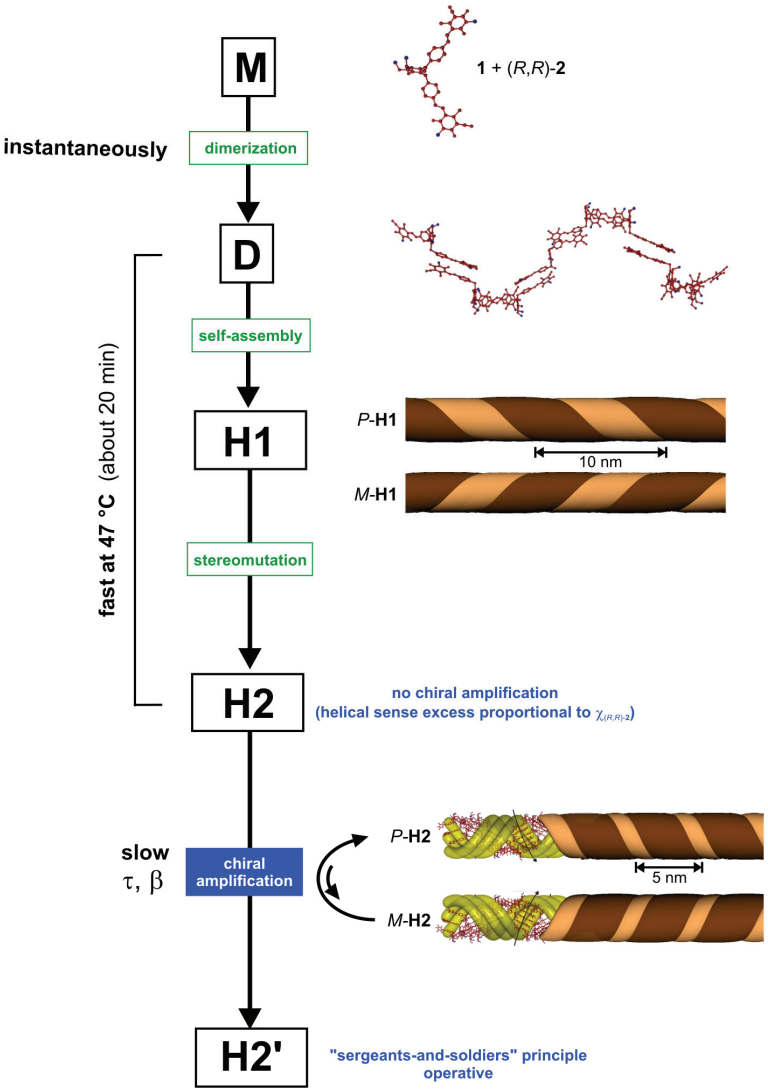

Fig. S1. Self-assembly sequence for mixtures of bis(merocyanine) dyes **1** and (*R*,*R*)-**2** with variable fraction of chiral (*R*,*R*)-**2** monomers into helical nanorods after initiation of the aggregation. Instantaneous dimerization of chromophores leads to oligomeric species **D**, which self-assemble into **H1** nanorods, and subsequently into **H2** nanorods.[S2] At elevated temperature (here 47 °C) this process is sufficiently fast compared to the subsequent chiral amplification process into **H2'** nanorods that is governed by the "sergeants-and-soldiers" principle. For the definition of τ and β, see next section.

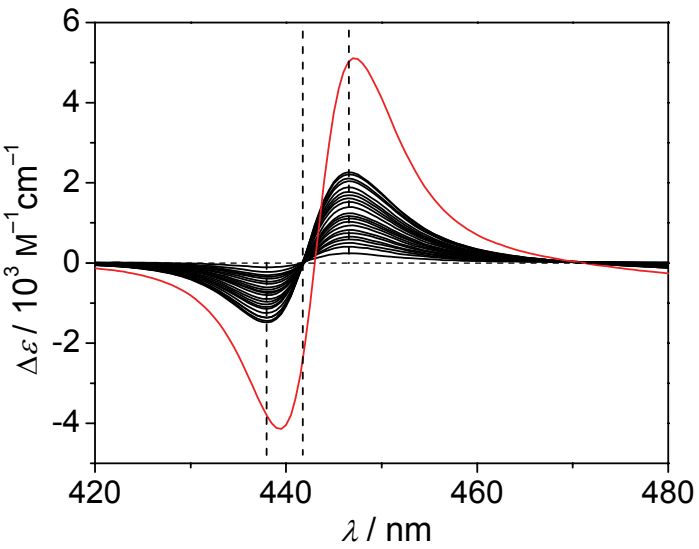

Fig. S2. Magnified section of the time-dependent CD spectra of nanorods formed from dyes **1** and (*R,R*)-**2** (95:5 mol%) shown in Fig. 2 (black solid lines), and for comparison the CD spectrum of **H2** aggregates formed from pure (*R,R*)-**2** monomers (red solid line). The dotted lines serve as an orientation for the spectral shifts.

2. Nonlinear curve fitting

After completed formation of **H2** nanorods at t_0, the time-dependent anisotropy factors $g(t)$ is composed of the anisotropy factor of **H2** nanorods before chiral amplification $g_{\mathbf{H2}}$ and that of **H2'** nanorods with operative chiral amplification $g_{\mathbf{H2'}}$ according to eq. S1, where $x(t)$ denotes the time-dependent fraction of monomers incorporated in nanorods with operative chiral amplification.

$$g(t) = g_{\mathbf{H2}} + \left(g_{\mathbf{H2'}} - g_{\mathbf{H2}}\right) \cdot x(t) \qquad \text{(S1)}$$

For the time-dependent fraction $x(t)$, a stretched exponential function was applied as given in equation S2, where t_0 denotes the initial time for completion of **H2** aggregate formation, τ the relaxation time, and β the stretching parameter. Notably, such stretched exponential kinetics with $\beta \approx 0.5$ are common for the empirical description of the relaxation phenomena of many physical properties of complex systems such as polymers and glasses, and are explained by a distribution of individual relaxation times.[S3]

$$x(t) = 1 - e^{-\left(\frac{t-t_0}{\tau}\right)^{\beta}} \qquad (t \geq t_0) \qquad \text{(S2)}$$

Combining equations S1 and S2 yields to eq. S3

$$g(t) = g_{\mathbf{H2'}} + \left(g_{\mathbf{H2}} - g_{\mathbf{H2'}}\right) \cdot e^{-\left(\frac{t-t_0}{\tau}\right)^{\beta}} \qquad (t \geq t_0) \qquad \text{(S3)}$$

The results obtained from nonlinear least square fitting of the time-dependent anisotropy factors g at 437 nm by equation S3 are collected in Table S1. Note, for this analysis the $g_{\mathbf{H2}}$ values were set as the expected g values in the absence of chiral amplification, that is, the g value for nanorods consisting of pure (*R*,*R*)-**2** ($g = -2.38\times10^{-2}$) multiplied by the respective fraction of chiral monomers $\chi_{(R,R)\text{-}\mathbf{2}}$.

Table S1. Results from curve fitting of the time-dependent g values

$\chi_{(R,R)\text{-}\mathbf{2}}$	g_{max} / 10^{-2}	τ / h	β	$r^{2\,a}$
5%	–1.93	68.9	0.47	0.9967
10%	–2.09	13.9	0.55	0.9998
20%	–2.12	3.1	0.68	0.9997

[a] Correlation coefficient

3. Additional References

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