## Supporting Information

# Thermo and Photoresponsive Behavior of Liquid-Crystalline Helical Structures with the Aid of Dual Molecular Motions 

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Scheme S1. Synthetic route for RBAC4, SBAC4, and C3OAC4



Figure S1. (A) Change in CD spectra of RBAC4 (solid line) and SBAC4 (dotted line) in 1,4-dioxane before (blue) and after irradiation (red) at $365 \mathrm{~nm}\left(6 \mathrm{mWcm}{ }^{-1}, 30 \mathrm{~s}\right)$ at room temperature. (B) Expansion of Figure S1(A) between 350 and 500 nm .

## Determination of Thermodynamic Parameters of cis to trans Isomerization Process

We investigated the thermal cis-trans isomerization process. For the thermal cis-trans isomerization,

$$
\begin{equation*}
\ln \frac{[c i s]}{[c i s]_{0}}=-k t \tag{1}
\end{equation*}
$$

where [cis] and $[c i s]_{0}$ are the concentrations of the cis-azobenzene at time $t$ and time zero, and $k$ is the rate constant for the thermal cis-trans isomerization. The first-order rate constant was determined by fitting the experimental data to the equation,

$$
\begin{equation*}
\ln \frac{A_{\infty}-A_{t}}{A_{\infty}-A_{0}}=-k t \tag{2}
\end{equation*}
$$

where $A_{t}, A_{0}$ and $A_{\infty}$ are the absorbance at 365 nm at time $t$, time zero and infinite time, respectively. The first order plots according to eq. 2 for the cis-trans thermal isomerization of RBAC4 and C3OAC4 as a model compound in 1,4-dioxane at various temperatures are shown in Figure S2.

Furthermore, thermodynamic parameters such as enthalpy of activation $\left(\Delta H^{*}\right)$ and entropy of activation $\left(\Delta S^{\dagger}\right)$ were determined according to the Eyring equation:

$$
\begin{equation*}
k=\frac{k_{B} T}{h} \exp \left(\frac{\Delta S^{\star}}{R}\right) \exp \left(-\frac{\Delta H^{*}}{R T}\right) \tag{3}
\end{equation*}
$$

where $R, k_{B}$, and $h$ are gas constant, Boltzmann constant, and Planck's constant, respectively. Substituting into eq. 3 ,

$$
\begin{equation*}
\ln \left(\frac{k h}{k_{B} T}\right)=-\frac{\Delta H^{\neq}}{R T}+\frac{\Delta S^{\neq}}{R} \tag{4}
\end{equation*}
$$

Figure S 3 shows Eyring plots for cis to trans thermal isomerization of RBAC4 and C3OAC4 in 1,4-dioxane. The values of $\Delta S^{\ddagger}$ and $\Delta H^{\star}$ were obtained from an intersect and a slope, respectively, of the linear plot of $\ln \left(k h / k_{B} T\right)$ versus $1 / T$ extrapolated to $T \rightarrow$ $\infty$.


Figure S2. First-order plots for cis to trans thermal isomerization of RBAC4 (A) and C3OAC4 (B) in 1,4-dioxane. (circle) $35^{\circ} \mathrm{C}$, (triangle) $45^{\circ} \mathrm{C}$, (square) $55^{\circ} \mathrm{C}$, and (cross) $65^{\circ} \mathrm{C}$, respectively.


Figure S3. Eyring plots for cis to trans thermal isomerization of RBAC4 (A) and C3OAC4 (B) in 1,4-dioxane.

Determination of Helical Pitch Length of Chiral Nematic Liquid Crystals (LC) by the Grandjean-Cano Method

To determine helical pitch length of the chiral nematic LC, we checked thermo and photoresponsive behavior of RBAC4 in the LC host by using the Grandjean-Cano method. Homogeneous LC alignment was
 conventionally achieved by rubbing mechanically a polyimide alignment layer coated on the substrate. In a wedge cell, the homogeneous alignment produces the typical

Grandjean-Cano texture with disclination lines. These lines indicate half pitch of the helical structure because of continuous change in length of the cell gap. We estimated each parameter under polarizing microscopic observation.

$$
\begin{equation*}
a=b \tan \theta \tag{5}
\end{equation*}
$$

where $a, b$, and $\theta$ are half length of the helical pitch, the distance between two disclination lines, and the angle of the wedge cell, $h / w$, determined by interference fringes in an empty cell. Pitch length $(p)$ was given by

$$
\begin{equation*}
p=2 a \tag{6}
\end{equation*}
$$

Substituting into eq.6,

$$
\begin{equation*}
p=2 b \tan \theta=2 b h / w \tag{7}
\end{equation*}
$$

