

# Supporting Information for

## Rewritable Optical Memory in Liquid Crystals Containing Photo-epimerizing Cr(III) Complexes

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**Materials:** Tris(acetylacetonato)chromium(III) ( $[\text{Cr}(\text{acac})_3]$ ) and (-)-3-(trifluoroacetyl)camphor (tfac(-)H) were used as purchased from Aldrich. ZLI-1132 (Merck) was used as received. The compound was stated to be a mixture of 4-(4-alkylcyclohexyl)benzotrile and 4-(4-alkylcyclohexyl)-4'-cyanobiphenyl derivatives ( $T_{\text{NI}} = 72.3 \text{ }^\circ\text{C}$ ; average molecular weight 263.2).

**Syntheses and purification of  $[\text{Cr}((-)\text{-tfac})_3]$ :** A free ligand (tfac(-)H) (0.75 g; 3 mmole) and  $[\text{Cr}(\text{acac})_3]$  (0.35 g; 1 mole) were mixed and kept in an autoclave for 16 hours at  $180 \text{ }^\circ\text{C}$ . The crude product was dissolved in benzene and eluted on a silica gel column (30 mm (i.d.) x 600 mm) with 1 : 9 (v/v) acetonitrile-benzene. From the mass spectral analyses, the first broad band was assigned to  $[\text{Cr}((-)\text{-tfac})_3]$  ( $m^+ / z = \text{obs. } 793; \text{calc. } 793$ ). The collected fraction was further purified by use of a chiral column as described below.

**Chromatographic separation of diastereomers:** The separation of diastereomeric isomers of  $[\text{Cr}((-)\text{-tfac})_3]$  from the first broad band collected on a silica gel column was performed chromatographically on a chiral column (4mm (i.d.) x 25cm; Ceramosphere RU-1 (Shiseido Co. Japan)). The column was packed with an ion-exchange adduct of  $\Delta\text{-}[\text{Ru}(\text{phen})_3]^{2+}$  (phen = 1,10-phenanthroline) and synthetic hectorite. The separated isomers were eluted again on the same column in order to check their purity.

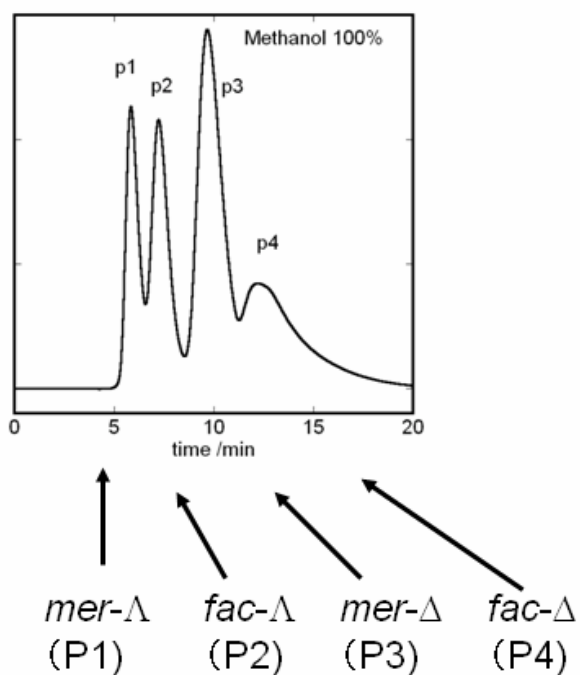


Figure S1. The HPLC chromatogram when a diastereomeric mixture of  $[Cr((-)-tfac)_3]$  was eluted on the chiral column. The elution was performed with methanol at a rate of  $1\text{ mL min}^{-1}$ . The monitoring was done by the absorbance at 600 nm.

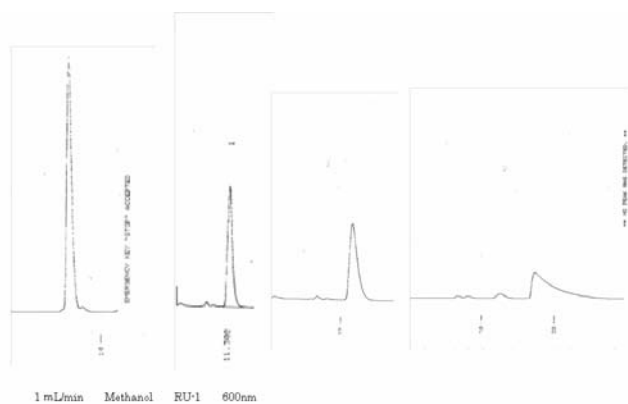


Figure S2. The HPLC chromatogram when the separated diastereomer of  $[Cr((-)-tfac)_3]$  was eluted on the chiral column again. The elution was performed under the same conditions as in Figure S1: P1, P2, P3 and P4 from left to right.

**$^1\text{HNMR}$  spectra of  $[Cr((-)-tfac)_3]$ :** The  $^1\text{HNMR}$  spectra of the enantiomeric diastereomers were measured as shown in Figure S3.

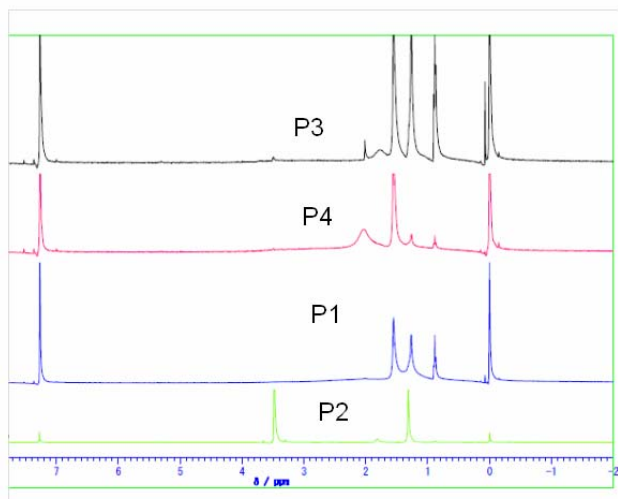


Figure S3. The  $^1\text{H}$ NMR spectra of the diastereomers of  $[\text{Cr}((-)\text{-tfac})_3]$  in  $\text{CDCl}_3$ . The determination of *mer*- or *fac*-configuration was made from the multiplicity of the peaks around  $\delta = 1.3$  assigned to  $\text{CH}_3$  protons in tfac ligands. The singlet peak was assigned to *fac*-isomers, while the triplet peaks were assigned to *mer*-isomers: P1 = *mer*- $\Lambda$ , P2 = *fac*- $\Lambda$ , P3 = *mer*- $\Delta$  and P4 = *fac*- $\Delta$

**Spectroscopic measurements:** The UV-vis and circular dichroism (CD) spectra were recorded on the methanol solutions of separated diastereomers. The measurements were done with a U-2810 spectrophotometer (Hitachi, Japan) and a J-720 spectropolarimeter (JASCO, Japan), respectively. The CD or UV-vis spectra of liquid crystal materials doping metal complexes were measured using a homogeneous alignment cell of 25  $\mu\text{m}$  thickness (RP type, EHC, Japan). HTP measurements were performed by the Cano method using a wedge cell (EHC, Japan). Temperature was controlled within an error of  $\pm 0.1$  by a Mettler FP82HT hot stage equipped with an FP90 control unit.

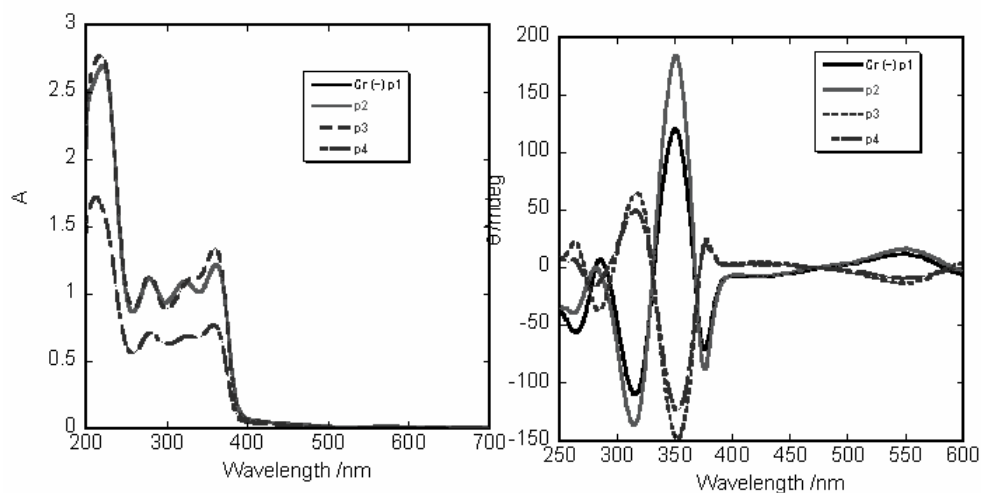


Figure S4. The UV-vis (left) and circular dichroism spectra (right) of the methanol solutions of the enantiomeric diastereomers of  $[\text{Cr}((-)\text{-tfac})_3]$ : P1 = *mer*- $\Lambda$  ( $5.0 \times 10^{-5}\text{M}$ ), P2 = *fac*- $\Lambda$  ( $5.0 \times 10^{-5}\text{M}$ ), P3 = *mer*- $\Delta$  ( $5.0 \times 10^{-5}\text{M}$ ) and P4 = *fac*- $\Delta$  ( $3.2 \times 10^{-5}\text{M}$ ).

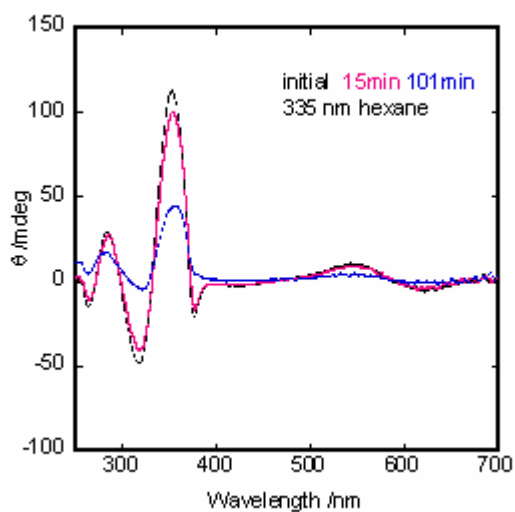
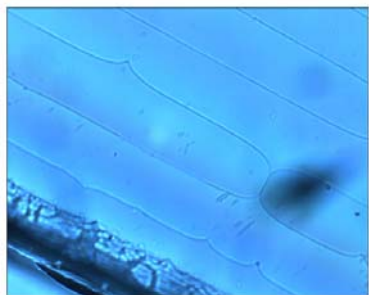
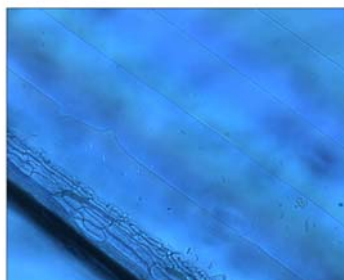


Figure S5. Circular dichroism spectra after the irradiation of a hexane solution of *mer*- $\Lambda$ - $[\text{Cr}((-)\text{-tfac})_3]$  at 335 nm ( $5.0 \times 10^{-5}\text{M}$ ).

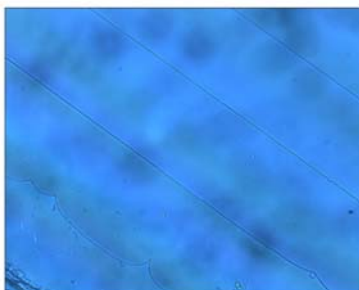
**Microscopic observation of the liquid crystal sample in a Cano wedge:** The liquid crystal sample (ZLI-1132 doping *mer*- $\Lambda$ -[Cr((-)-tfac)<sub>3</sub>] at 0.4 % molar ratio) was injected into a Cano wedge cell (KCRS-07; (EHC, Japan)). The sample was observed with a microscope by 20 times magnification.



(a)



(b)

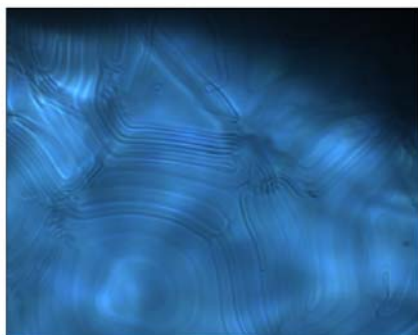


(c)

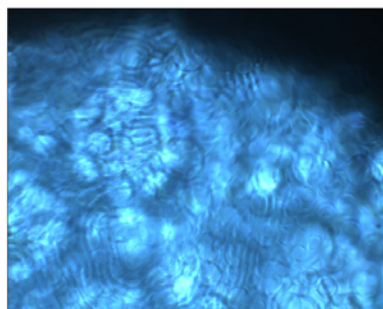
Figure S6. The image of the microscopic observation on the liquid crystal samples (ZLI-1132/*mer*- $\Lambda$ -[Cr((-)-tfac)<sub>3</sub>] under illumination of light at 365 nm: (a) before irradiation; (b) irradiated at 365 nm for 6 minutes; (c) irradiated at 365 nm for 30 minutes.

**Microscopic observation of the phase transformation of liquid crystal to isotropic medium:** A

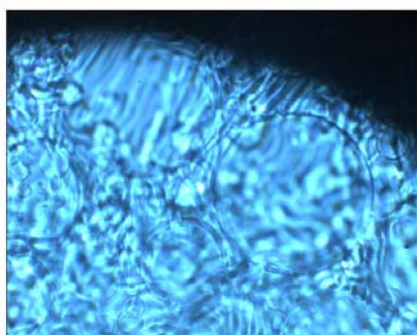
drop of liquid crystal sample (ZLI-1132 doping *mer*- $\Lambda$ -[Cr((-)-tfac)<sub>3</sub>] at 0.4 % molar ratio) was placed onto a glass plate and observed with a microscope (20 magnification) by raising temperature.



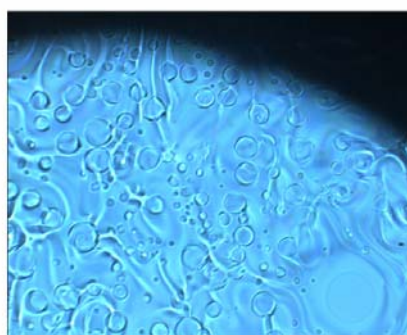
(a)



(b)



(c)



(d)

Figure S7. The image of the microscopic observation on the liquid crystal samples (ZLI-1132/*mer*- $\Lambda$ -[Cr((-)-tfac)<sub>3</sub>]) at various temperature: (a) 57.5 °C; (b) 73.5 °C; (c) 75.8 °C; (d) 78.0 °C. The rate of temperature rise was 1 °C per minute.