Electronic Supplementary Information to:

Isolation and Photo Transformation of Enatiomerically Pure Iridium(III) Bis[(4,6-difuorophenyl)pyridinato-N,C^2]picolinate

Yue Wang,[1] Takunori Harada,[2] Yoshihito Shiota,[3] Kazunari Yoshizawa,[3] Heng Wang,[1] Shen Wang,[1,†] Xichong Ye,[1,†] Masamichi Ogasawara,[4] and Tamaki Nakano[1,5,*]

[1]*Institute for Catalysis and Graduate School of Chemical Sciences and Engineering, Hokkaido University, N21 W10, Kita-ku, Sapporo 001-0021*

[2]*Department of Applied Chemistry, Faculty of Engineering, Oita University, 700, Dannoharu, Oita,Oita 870-1124, Japan*

[3]*Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan*

[4]*Graduate School of Science and Technology, Tokushima University, 2-1, Minamijosanjima-cho, Tokushima 770-8506, Japan*

[5]*Integrated Research Consortium on Chemical Sciences (IRCCS), Institute for Catalysis, Hokkaido University, N21W10, Kita-ku, Sapporo 001-0021, Japan*

[†]On leave from College of Chemistry & Molecular Engineering, Peking University as visiting students

*(*E-mail: tamaki.nakano@cat.hokudai.ac.jp).*

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Experimental

Materials. Iridium(III) Bis[(4,6-difuorophenyl)pyridinato-N,C^2]picolinate (FIrpic) was purchased from Sigma-Aldrich and used as obtained. Chromatographic eluents were used as obtained.

Instrumentation and measurements. Analytical HPLC resolution was performed using a JASCO's chromatraphic setup consisting of a DG-980-50 degasser, a PU-980 pump, a UV-2070 detector, and a CD-2095plus detector equipped with a Daicel ChiralPak IA column or IC column (25 cm x 0.42 cm (i.d.)). Preparative HPLC resolution was conducted using JASCO PU-2086/UV-2075/RI-2031 equipped with a Daicel ChiralPak IC column (25 cm x 2 cm (i.d.)). Circular dichroism (CD) spectra were taken with a JASCO-820 spectrometer. UV-vis absorption spectra were measured on a JASCO V-570 spectrophotometer. Emission spectra were taken using a JASCO FP-8500 fluorescence spectrophotometer. FT-IR spectra were measured with a JASCO FT/IR6100 spectrometer. Photo irradiation was performed using an Ushio Optical Modulex SX-UID500MAMQQ 500-W Hg-Xe lamp equipped with a quartz-made collimating lens with a Gran-Taylor prism to obtain linearly polarized light (LPL) (ca. 40 mW/cm^2) or without any prism to obtain non-polarized light (NPL) (ca. 200 mW/cm^2). The distance between the source light and the sample was 35 cm. The light power was measured using a Coherent PM10 thermal sensor with a Coherent FieldmaxII-TO power meter.

CPL emission measurements. Circularly polarized luminescence (CPL) and nonpolarized fluorescence spectra were measured by using a dual-purpose CD and CPL spectrophotometer (J-700CPL) equipped with Stokes-Mueller matrix analysis system.[1] The excitation wavelength was set to 286 nm and the emission wavelengths were recorded over a wavelength range of 600–420 nm with 3 mm slit width and 10 nm spectral bandwidth for the excitation and emission monochromators, respectively. For the solid-state CPL measurements, artifact-free CPL spectra were measured carefully for both enantiomeric films (FIrpic 1 and 2 films), employing the set of procedures based on Stokes–Mueller matrix equations to remove parasitic artifacts.

Computational method. Geometrical optimization of iridium complexes without any symmetry constraint was carried out with the B3LYP functional[2,3] in the Gaussian 09 program package.[4] The SDD basis[5] for Ir atom and the 6-311+G* basis[6] for C, N, O, F, and H atoms were used, The electronic excitation energies, rotational strengths of the iridium complexes have been calculated using time-dependent density functional theory (TDDFT).[7] Rotational strengths were calculated using the velocity representation.[8] In comparison of calculated ECD spectra with experimental spectra, Gaussian bandshapes with a bandwidth of 0.25 eV were used to simulate the UV–Vis and ECD spectra.

Chromatographic resolution of FIrpic using a Daical ChiralPak IA column hexane/2-propanol or hexane/2-propanol/CH_2Cl_2 as eluent

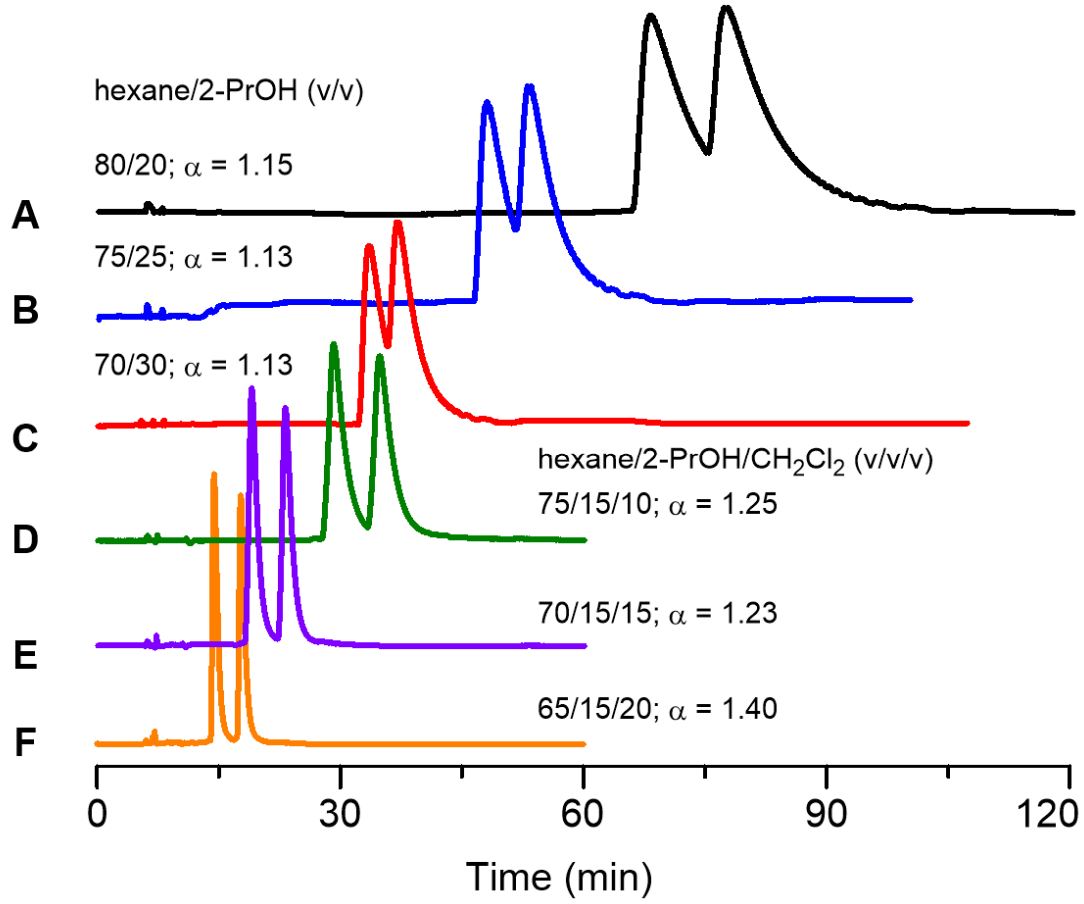
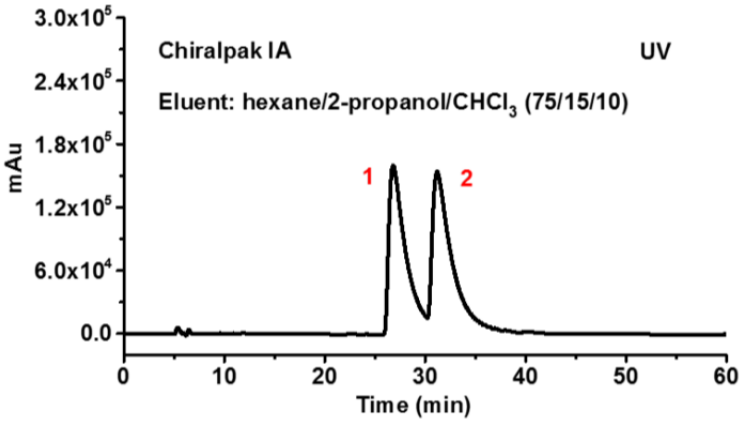


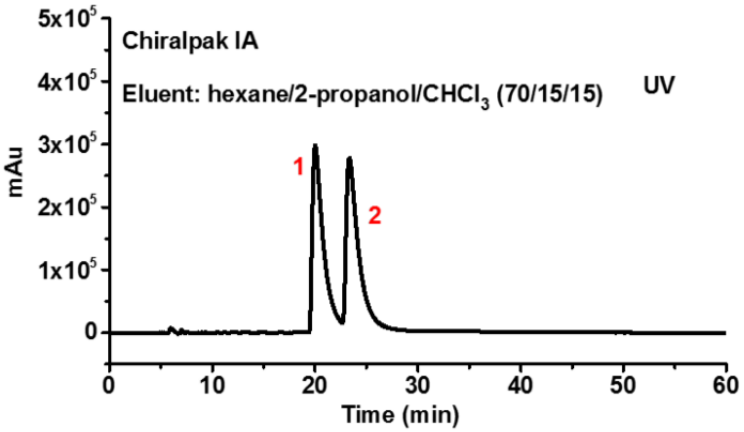
Figure S1. HPLC resolution profiles of FIrpic obtained using a Daicel ChiralPak IA column (25 cm x 0.46 cm (i.d.)) with binary (hexane/2-pronanol (A-C)) and ternary (hexane/2-pronanol/CH_2Cl_2 (D-F)) eluent systems where α denotes separation factor. HPLC conditions: flow rate = 0.5 ml/min, detection = UV at 250 nm.

Chromatographic resolution of FIrpic using a Daical ChiralPak IA column hexane/2-propanol/$CHCl_3$ as eluent

A. hexane/2-propanol/$CHCl_3$ = 75/15/10 (v/v/v); α = 1.21



B. hexane/2-propanol/$CHCl_3$ = 70/15/15 (v/v/v); α = 1.28



C. hexane/2-propanol/$CHCl_3$ = 65/15/20 (v/v/v); α = 1.29

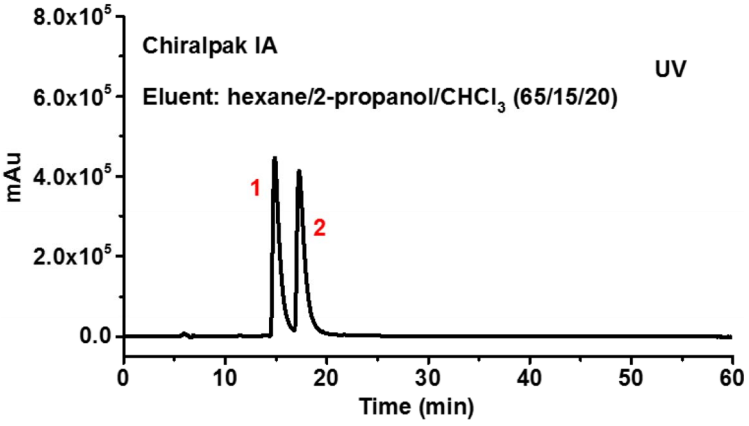


Figure S2. HPLC resolution profiles of FIrpic obtained using a Daicel ChiralPak IA column (25 cm x 0.46 cm (i.d.)) with ternary (hexane/2-pronanol/chloroform) eluent systems α denotes separation factor. HPLC conditions: flow rate = 0.5 ml/min, detection = UV at 254 nm.

Chromatographic resolution of FIrpic using a Daical ChiralPak IC column under various eluent conditions

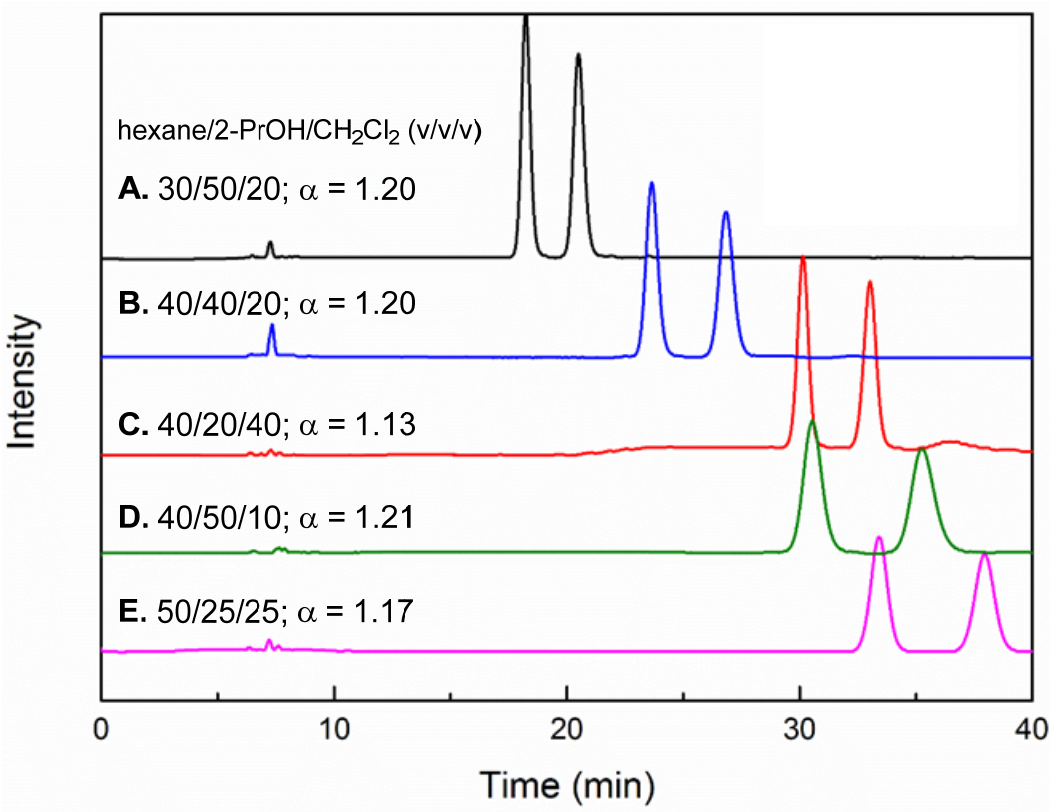


Figure S3. HPLC resolution profiles of FIrpic obtained using a Daicel ChiralPak IC column (25 cm x 0.46 cm (i.d.)) with ternary hexane/2-pronanol/dichloromethane eluent systems at various ratios where α denotes separation factor. HPLC conditions: flow rate = 0.5 ml/min, detection = UV at 254 nm.

Chromatographic resolution of FIrpic using a Daical ChiralPak OD column under various eluent conditions

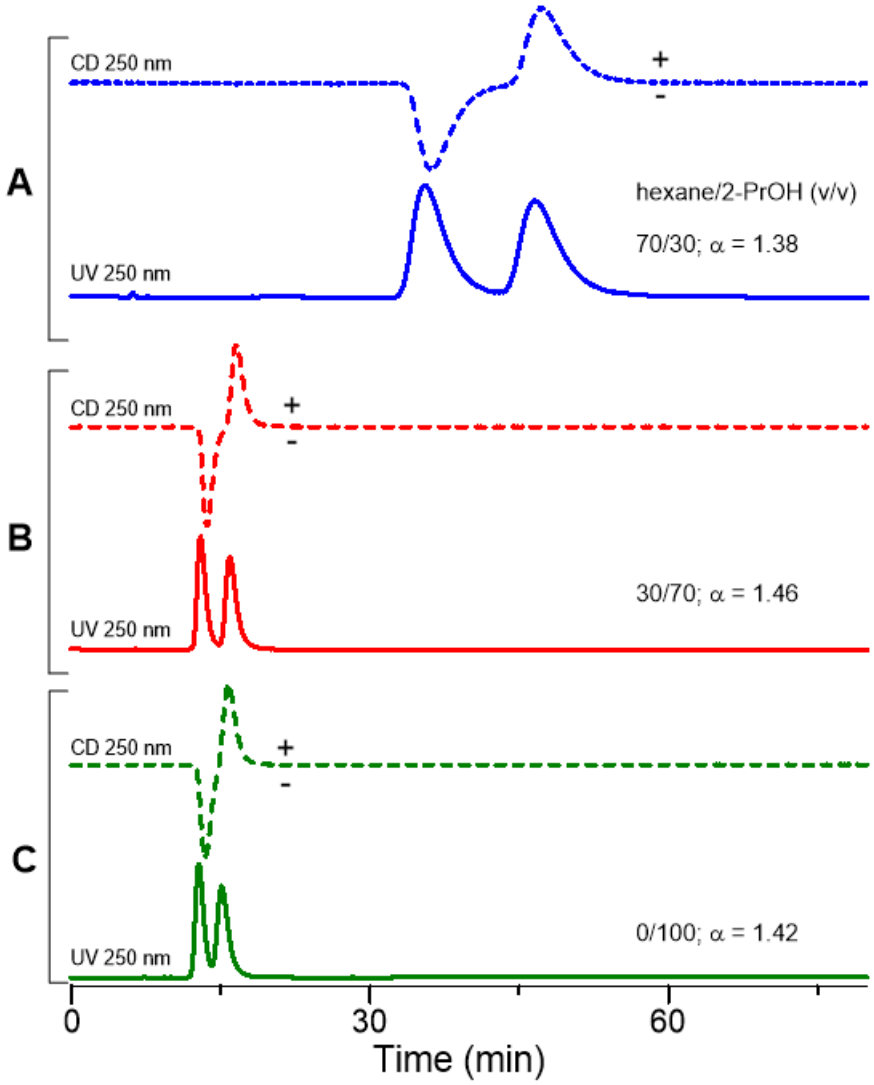


Figure S4. HPLC resolution profiles detected with CD and UV (top and bottom of each, respectively) of FIrpic obtained using a Daicel ChiralPak OD column (25 cm x 0.46 cm (i.d.)) with binary hexane/2-pronanol eluent systems (A, B) and with pure 2-PrOH as eluent (C) where α denotes separation factor. HPLC conditions: flow rate = 0.5 ml/min, detection = UV at 250 nm.

*The CD signs of the first- and second-eluted isomer were opposite to those reported in ref. 9 under the same separation condition.

Comparison of theoretical and experimental CD spectra

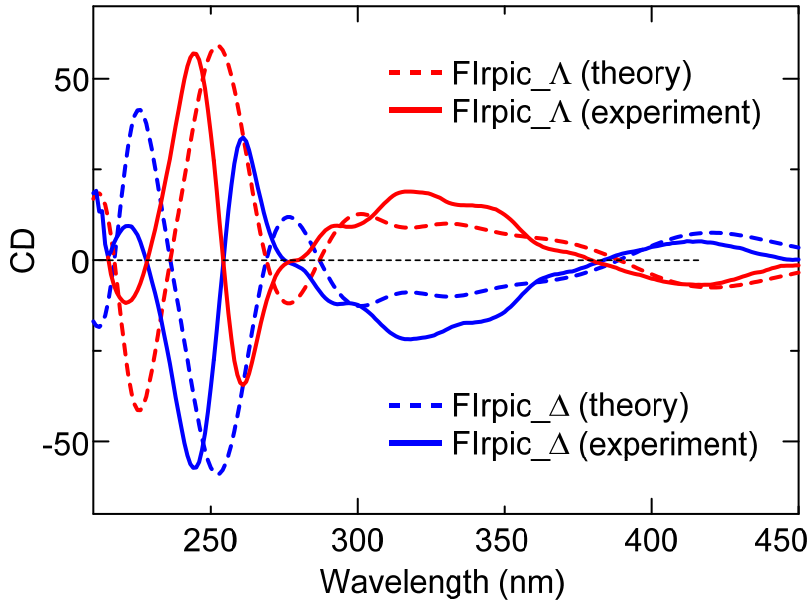
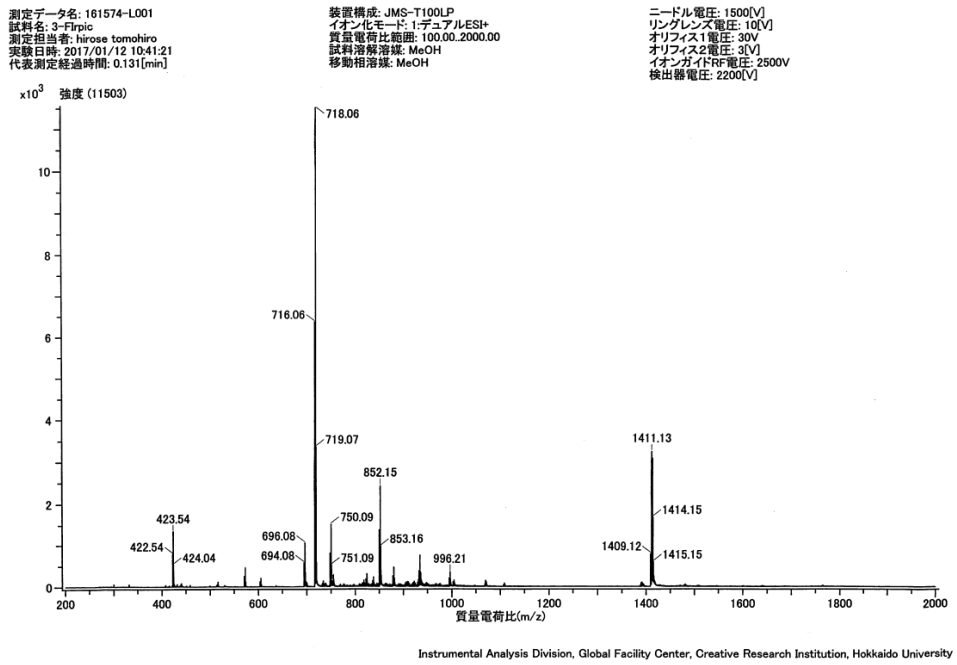


Figure S5. Theoretical and experimental CD spectra of the Δ- and Λ-isomers. The experimental spectra were taken in MeOH at room temperature at 5.0 x 10^{-5} M in a 1-mm cell.

Mass spectra

A



B

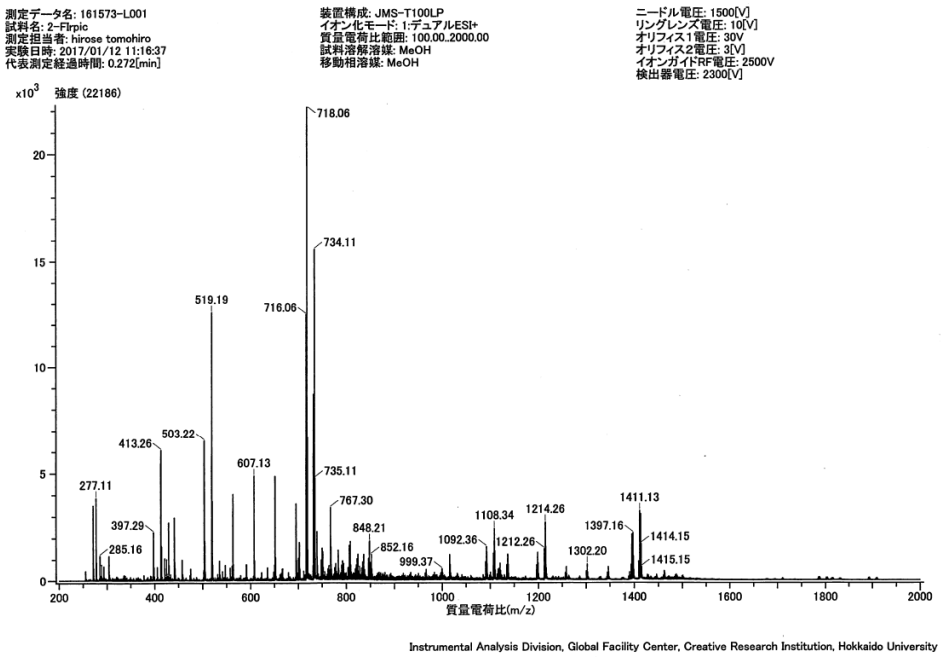
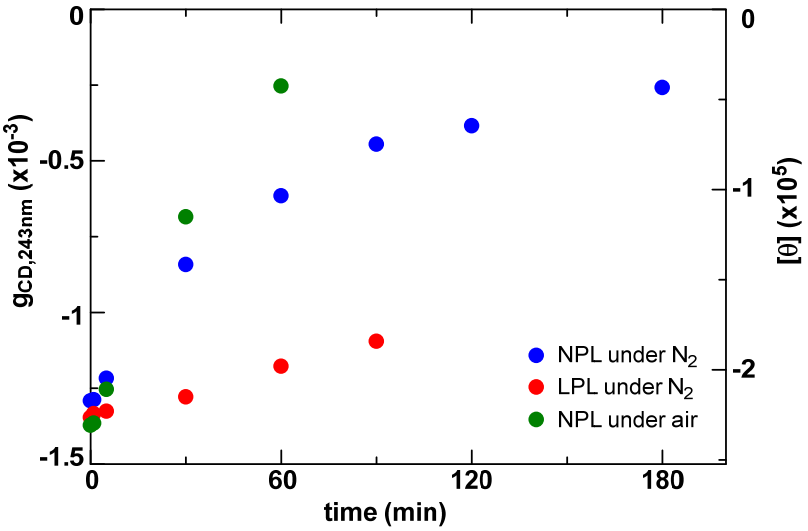


Figure S6. ESI mass spectra of rac-FIrpic (A) and the optically active, photo-transformation product isolated by HPLC (B).

A



B

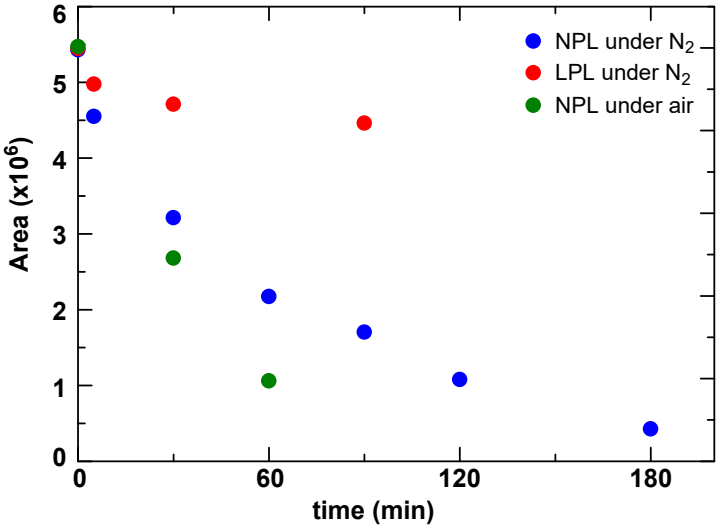


Figure S7. g_{CD}-vs.-irradiation (A) and HPLC peak area of L-isomer-vs.-irradiation time (B) plots for the experiments using NPL (ca. 200 mW/cm^2) under N_2 (blue circle), LPL (ca. 40 mW/cm^2) under N_2 (red circle), and NPL (ca. 200 mW/cm^2) under air (green circle).

Reference

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