Electronic Supporting Information

for

Photochirogenesis in chiral ionic liquid: Enantiodifferentiating [4+4] photocyclodimerization of 2-anthracenecarboxylic acid in 
(R)-1-methyl-3-(2,3-dihydroxypropyl)imidazolium bistriflimide

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Experimental

Instruments. UV/vis and CD spectra were recorded on JASCO V-560 and J-720WI or J-820 spectrometers equipped with JASCO ETC-505T or UNISOKU USP-203CD cryostat. NMR spectra were recorded on a Bruker Avance 250 Instrument. ESI-MS analyses were performed on a Finnigan LQC Advantage ion-tap instrument equipped with Excalibur software. Chiral HPLC analysis was run on a JASCO HPLC system fitted with an FP-2025 fluorescence detector (λex = 254 nm, λem = 420 nm).1

Materials. All chemicals were reagent grade and used as received, except for 1-methyl-1H-imidazole, which was distilled under argon before use.

AC salts were prepared as follows. Equimolar amounts of 2-anthracenecarboxylic acid (AC-H) and alkali metal hydroxide (LiOH, KOH, CsOH) were dissolved in distilled water and the mixture was stirred for 3 d. The solution was freeze-dried to give the corresponding AC salts as yellow powder.

(R)-1-Methyl-3-(2,3-dihydroxypropyl)imidazolium chloride was prepared as previous reported for the corresponding racemic compound. 2 (R)-1-Methyl-3-(2,3-dihydroxypropyl)imidazolium bistriflimide ([glymim][Tf2N]) was obtained by mixing (R)-1-(2,3-dihydroxypropyl)-3-methyl-1H-imidazolium chloride (10 g, 52 mmol) with lithium bistriflimide (15.1 g, 53 mmol) in water (70 mL). The solution was stirred at room temperature overnight and then dichloromethane was added. The resulting mixture was stirred vigorously and maintained at room temperature until a three-phase system, composed of chiral ionic liquid (CIL), dichloromethane and water-LiTf2N-CIL, was obtained. The separated CIL was dissolved again in
water and the procedure was repeated three times. The dried CIL (11.3 g, 55% yield) was obtained as a pale yellow oil. $^1$H NMR (neat, 70 °C): $\delta$ 7.84 (1H, s), 6.75 (1H, t, $J = 1.7$ Hz), 6.66 (1H, t, $J = 1.7$ Hz), 3.64 (1H, dd, $J = 14.1$ Hz, $J = 3.2$ Hz), 3.51 (1H, dd, $J = 14.1$ Hz, $J = 7.6$ Hz), 3.36 (1H, m), 3.19 (3H, s), 2.94 (2H, m). $^{13}$C NMR (neat, 70 °C): $\delta$ 134.6 (CH), 121.5 (CH), 121.3 (CH), 117.9 (CF$_3$ q, $J = 321$ Hz), 68.3 (CH), 61.2 (CH$_2$), 50.2 (CH$_2$), 33.8 (CH$_3$). ESI-MS (CH$_3$OH): $m/z$ 157.7 (glymim$^-$); 280 (Tf$_2$N$^-$).

**Sample preparation and photolysis procedures.** AC-X was added to neat CIL in a test tube, and the mixture was sonicated for 10 min. The resulting suspension was filtered to give a transparent CIL solution saturated with AC-X, which was subjected to the spectroscopic measurement and photoreaction. The saturated CIL solution of AC-X (ca. 200 μL) placed in a quartz cell (1 x 10 x 45 mm) was irradiated for 3 h at temperatures ranging from 25 to –50 °C under aerated conditions, by using a 500-W ultrahigh-pressure mercury lamp fitted with a UV-35 glass filter. An aqueous solution of 2 mM NaOH (200 μL) was added to the photolyzed sample to give a homogeneous solution, to which was added acetonitrile (100 μL). A 5 μL aliquot was analyzed by chiral HPLC equipped with a tandem column of Nakalai Cosmosil 5C18-AR-II and Daicel Chiralcel OJ-RH eluted by a 64:36 (v/v) water-acetonitrile mixture to determine the distribution and enantiomeric excesses of photocyclodimers.$^1$

**UV/vis and CD spectra of AC-K and AC-Cs in CIL**

![Figure S1](https://example.com/fig.png)

**Figure S1.** UV/vis and CD spectra of a saturated (a) AC-K and (b) AC-Cs in CIL at 25 °C (black), 0 °C (red) and –50 °C (blue), measured in a 0.1 mm cell; measurement in a 1 mm cell gave less reliable CD spectrum due to the opaque CIL solution.

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