

**Supporting Information for: Optical Isomers of *N,N'*-bis(1-phenylethyl)-2,6-pyridinedicarboxamide Coordinated to Europium(III) Ions as Reliable Circularly Polarized Luminescence Calibration Standards**

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**Experimental Section.**

**General.** Solvents and starting materials were purchased from Aldrich or Acros and used without further purification unless otherwise stated. (+/-)-( $\alpha$ )-Methylbenzylamine<sup>1</sup> was vacuum distilled from sodium hydroxide and dried overnight over 3A molecular sieves before use. Europium trifluoromethanesulfonate, Eu(Otf)<sub>3</sub>, was prepared from the europium oxide (Stanford Materials Corporation, 99.995%) and dried according to published procedures.<sup>2</sup> The Ln content of solutions was determined by complexometric titrations with Titriplex III (Merck) in the presence of urotropine and xylene orange.<sup>3</sup>

**Spectroscopic Measurements.** IR spectra were obtained from samples dispersed in nujol with a Maxim Satellite FT-IR spectrometer. Optical rotation values were measured from  $6.67 \times 10^{-3}$  M solution in anhydrous acetonitrile at 298 K with the help of a Rudolph Autopol III polarimeter (sodium D line).  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra and experiments ( $\{^1\text{H}-^1\text{H}\}$  COSY,  $\{^1\text{H}-^{13}\text{C}\}$  HSQC, and DEPT-135) were performed on a 300 MHz Mercury NMR spectrometer. Chemical shifts are given in ppm with respect to TMS. GC-MS data were obtained using an Agilent Technologies 6890N GC 5975B MSD instrument. Elemental analyses were conducted at Desert Analytics, Inc (Tucson, AZ).

Circularly polarized luminescence and total luminescence spectra were recorded on an instrument described previously.<sup>4</sup> A circular analyzer consisting of an oscillating photo-elastic polarization modulator (PEM) followed by a high quality linear polarizer, is located between the emitting sample and the emission monochromator. This circular analyzer allows detecting the net circular polarization in the luminescence. Detection of the alternating emitted left and right polarization light is accomplished by a thermoelectrically cooled photomultiplier tube (PMT), operating in a differential photon-counting mode. The photo-pulses corresponding to the intensity of left and right circularly polarized emitted light are collected by two separate digital counters. It should be added that various elements including linear polarizers, sample containers, filters, mirrors, the PEM which is not a perfect optical element, etc. may lead to systematic sources of error. The standard deviation,  $\sigma_d$ , in the measurement of the luminescence dissymmetry factor,  $g_{\text{lum}}$ , is defined as follows:

$$\sigma_d = \sqrt{\frac{2}{N}}$$

where  $N$  is the total number of photon-pulses counted. One can see that the determination of accurate  $g_{\text{lum}}$  values can be done in a short time for transitions associated with large  $g_{\text{lum}}$  values of highly luminescent compounds, whereas a longer time of collection is required for transitions associated with small  $g_{\text{lum}}$  values of weakly luminescent systems for achieving the same percent error. As the time required for measuring a CPL spectrum is dependent on the intensity of the luminescence of the system of interest and the “chirality” of the transition analyzed, the photo-pulses are collected for the same amount of time at each wavelength. As a result, the relative error at each of these wavelengths is the same in the CPL spectrum measured. The light source for excitation was a continuous wave 450 W Xenon arc lamp from a Spex FluoroLog-2 spectrofluorimeter, equipped with excitation and emission monochromators with dispersions of 4 nm/mm (SPEX, 1681B).

${}^5\text{D}_0 \leftarrow {}^7\text{F}_0$  Excitation measurements for the Eu(III)-containing compounds were accomplished by using a Coherent-599 tunable dye laser (0.03 nm resolution) with a Coherent Innova Sabre TMS 15 or Innova-70 argon ion laser as a pump source. The laser dye used in all measurements was rhodamine 6G dissolved in ethylene glycol. Calibration of the emission monochromator (and subsequently the dye laser wavelength) was accomplished by passing scattered light from a low power He-Ne laser through the detection system. The error in the dye-laser wavelength is assumed to equal the resolution of the emission monochromator (0.1 nm). The optical detection system consisted of a focusing lens, long pass filter, and 0.22 m monochromator. The emitted light was detected by a cooled EMI-9558B photo-multiplier tube operating in photon-counting

mode. All measurements were performed in quartz cuvettes with a path length of 0.4 or 1.0 cm.

**Preparation of the optical isomers of *N,N'*-bis(1-phenylethyl)-2,6-pyridinedicarboxamide.**

**(*S,S*)-*N,N'*-bis(1-phenylethyl)-2,6-pyridinedicarboxamide ((*S,S*)-1).** A solution of 13.8 mL (13.1 g, 107.8 mmol) of (*S*)-(-)-( $\alpha$ )-methylbenzylamine (99+% e.e.) was added to a stirring mixture of 500 mL CH<sub>2</sub>Cl<sub>2</sub> and 500 mL 5% sodium bicarbonate. 2,6-Pyridinedicarboxylic acid chloride (10.0 g, 49.0 mmol) was added to the mixture and vigorous stirring was continued for 1 hour. The organic layer was separated, extracted with 2  $\times$  75 mL 5% sodium bicarbonate, dried over sodium sulfate and filtered. Solvent was removed at high vacuum for 45 minutes in a warm water bath. Recrystallization was performed by dissolving the solids in a warm mixture of 400 mL hexane and 200 mL chloroform. The mixture was then cooled at -20° C overnight and collected on a pre-cooled medium glass frit. The white needles were washed with cold pentane (3  $\times$  75 mL) and dried under vacuum. Additional material was isolated from the mother liquor. The combined solids were dried under high vacuum for an hour to reach constant weight (16.4 g, 44.0 mmol, 90%). Mp. 141.1-142.1° C. <sup>1</sup>H-NMR in CDCl<sub>3</sub>:  $\delta$  1.65 (d, 6H,  $J$  = 7.0 Hz), 5.31 (q, 2H,  $J$  = 7.1 Hz), 7.37 (m, 10H), 7.83 (d, 2H,  $J$  = 7.9 Hz), 8.03 (t, 1H,  $J$  = 7.8 Hz), 8.35 (d, 2H,  $J$  = 7.0 Hz). <sup>13</sup>C NMR in CDCl<sub>3</sub>:  $\delta$  22.1 (2C), 49.4 (2C), 125.4 (2C), 126.3 (4C), 127.9 (2C), 129.1 (4C), 139.4 (1C), 143.1 (2C), 148.9 (2C), 162.7 (2C). DEPT-135: CH<sub>3</sub> (22.1) and CH (49.4, 125.4, 126.3, 127.9, 129.1, 139.4). IR  $\nu$ (cm<sup>-1</sup>, nujol): 3307-3292, 1676, 1640, 1515. EI-MS (MeCN):  $m/z$  373.0 ([M]<sup>+</sup>). GC at 275° C in

toluene, RT 5.885 min. Optical rotation  $[\alpha]_D^{20}$  (6.67 mM, CH<sub>3</sub>CN): +213.6°. C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>: calcd. C 73.9, H 6.2, N 11.2; found C 73.2, H 6.5, N 11.1.

**(*R,R*)-*N,N'*-bis(1-phenylethyl)-2,6-pyridinedicarboxamide ((*R,R*)-1).** This compound was synthesized following the same experimental procedure as (*S,S*)-**1** using (*R*)-(+)-( $\alpha$ )-methylbenzylamine (99+% e.e.) (16.7 g, 44.8 mmol, 91%). Mp. 141.1-142.1° C. <sup>1</sup>H-NMR in CDCl<sub>3</sub>:  $\delta$  1.65 (d, 6H, *J* = 7.0 Hz), 5.31 (q, 2H, *J* = 7.1 Hz), 7.37 (m, 10H), 7.83 (d, 2H, *J* = 7.9 Hz), 8.03 (t, 1H, *J* = 7.8 Hz), 8.35 (d, 2H, *J* = 7.0 Hz). <sup>13</sup>C NMR in CDCl<sub>3</sub>:  $\delta$  22.1 (2C), 49.4 (2C), 125.4 (2C), 126.3 (4C), 127.9 (2C), 129.2 (4C), 139.3 (1C), 143.1 (2C), 148.9 (2C), 162.7 (2C). DEPT-135: CH<sub>3</sub> (22.1) and CH (49.4, 125.4, 126.3, 127.9, 129.1, 139.3). IR  $\nu$ (cm<sup>-1</sup>, nujol): 3300-3293, 1673, 1639, 1515. EI-MS (MeCN): *m/z* 373.0 ([M]<sup>+</sup>). GC at 275° C in toluene, RT 5.805 min. Optical rotation  $[\alpha]_D^{20}$  (6.67 mM, CH<sub>3</sub>CN): -213.4°. C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>: calcd. C 73.9, H 6.2, N 11.2; found C 73.6, H 6.4, N 11.2.

**(*R,S*)-*N,N'*-bis(1-phenylethyl)-2,6-pyridinedicarboxamide ((*R,S*)-1).** A similar experimental procedure to (*S,S*)-**1** was used to synthesize (*R,S*)-**1** with (+/-)-( $\alpha$ )-methylbenzylamine. However, several recrystallizations were required to isolate (*R,S*)-**1** by fractional crystallization. The solids were dissolved in warm toluene (6.6 mg/mL) while stirring and the solution was cooled to 0° C overnight. Crystals were collected on a pre-cooled medium frit and rinsed with small portions of cold toluene solution. The mixture of isomers is conveniently assayed by <sup>1</sup>H NMR in C<sub>6</sub>D<sub>6</sub>; the methyl doublets are fully resolved in this solvent ( $\delta$  1.32 ppm for (*R,S*)-**1** vs. 1.26 ppm for (*R,R*)-**1** and (*S,S*)-**1**) and integration of these peaks gives the ratio of isomers directly. Purity of 97.8% was obtained after four recrystallizations before drying to constant weight (4.9 g, 13.1 mmol,

28%). Mp. 228.1-229.1° C. <sup>1</sup>H-NMR in CDCl<sub>3</sub>: δ 1.62 (d, 6H, *J* = 7.3 Hz), 5.31 (q, 2H, *J* = 6.8 Hz), 7.35 (m, 10H), 7.85 (d, 2H, *J* = 6.5 Hz), 8.03 (t, 1H, *J* = 7.6 Hz), 8.34 (d, 2H, *J* = 7.6 Hz). <sup>13</sup>C NMR in CDCl<sub>3</sub>: δ 22.2 (2C), 49.2 (2C), 125.1 (2C), 126.0 (4C), 127.6 (2C), 128.9 (4C), 139.1 (1C), 142.9 (2C), 148.8 (2C), 162.8 (2C). IR ν(cm<sup>-1</sup>, nujol): 3354-3280, 1676, 1643, 1525. EI-MS (MeCN): *m/z* 373.0 ([M]<sup>+</sup>). GC at 275° C in toluene, RT 5.513 min. Optical rotation [ $\alpha$ ]<sub>D</sub><sup>20</sup> (6.67 mM, CH<sub>3</sub>CN): -0.8°. C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>: calcd. C 73.9, H 6.2, N 11.2; found C 73.5, H 6.6, N 11.1.

## References.

- 1 Matheson Coleman & Bell, ( $[\alpha]_D^{20} = +1.03^\circ$ ). There is a slight excess of (*R*)-( $\alpha$ )-methylbenzylamine in the stock solution.
- 2 (a) J.-C. G. Bünzli and C. Mabillard *Inorg. Chem.*, 1986, **25**, 2750. (b) J.-C. G. Bünzli and F. Pilloud *Inorg. Chem.*, 1989, **28**, 2638.
- 3 G. Schwarzenbach, *Complexometric Titrations*; Chapman & Hall: London, 1957, p. 8.
- 4 J. P. Riehl and G. Muller, in *Handbook on the Physics and Chemistry of Rare Earths*; ed. K. A. Gschneidner Jr., J.-C. G. Bünzli, V. K. Pecharsky, North-Holland Publishing Company: Amsterdam, 2005, vol. 34, ch. 220, pp. 289–357.