

# Designed Synthesis and Crystallization of Isomorphous Molecular Gyroscopes with Cell-like Bilayer Self-Assemblies

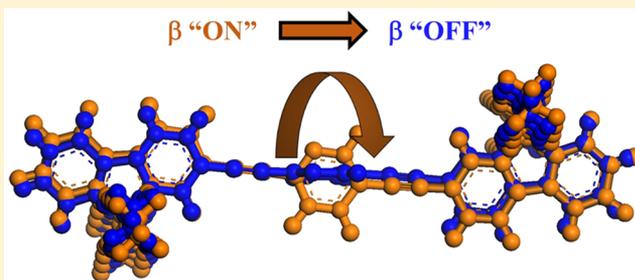
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## Supporting Information

**ABSTRACT:** Two molecular rotors featuring pyridine and fluorobenzene rings as polar rotators and 9-octylfluorenyl stators were synthesized. Their crystal structures were established through SXRD techniques, crystallizing in the monoclinic chiral  $P2_1$  space group. The supramolecular assemblies of both isomorphs showed an orientation of static dipoles through the crystal lattice and the formation of intriguing 2D layers that resemble cell membranes, a typical example of an amphidynamic system. Small activation energies and the modulation of the first-order hyperpolarizabilities of these compounds as a function of rotational dynamics were revealed through DFT computations at the CAM-B3LYP/M06-2X/cc-pVDZ level of theory and correlated with a potential use of these materials as photonic switches.



## 1. INTRODUCTION

Amphidynamic systems, defined as 3D molecular arrays that, despite their long-range phase order, also display fast molecular dynamics, have the potential to act as molecular rotors, i.e., crystalline molecular machines that, when properly engineered, may display efficient rotational work such as that of macroscopic gyroscopes or compasses.<sup>1</sup> These crystal systems, expected to display interesting properties like dichroism and birefringence,<sup>2</sup> usually incorporate a 1,4-diethynylphenylene ring linked at both ends to rigid frameworks that provide the supramolecular information that dictates the crystal packing.

Our group of work has put intense collaborative efforts in studying the rotational dynamics of molecular rotors possessing diverse rigid steroidal frameworks linked through acetylenic axles to 1,4-phenylene rotators.<sup>3–5</sup> During the course of these investigations, the possibility of controlling the rotational dynamics of these molecular compasses like systems using a magnetic stimulus became appealing.

Herein, we describe the synthesis and supramolecular structure of molecular rotors featuring 9,9-dioctylfluorene groups as stators and pyridine and fluorobenzene rings as polar rotators. The static dipolar moments present in these molecules are intended to facilitate control of rotational dynamics upon application of an external magnetic field. Through SXRD analysis of these systems, we found that they present peculiar solid-state self-assemblies that resemble closely cell membranes, as well as other supramolecular features that make these crystalline isomorphs interesting systems to be studied as molecular gyroscopes.

## 2. EXPERIMENTAL SECTION

**2.1. General Experimental Considerations. Materials.** All starting materials were purchased from Sigma-Aldrich and used without further purification. Solvents were purified by distillation over appropriate drying agents. Compounds 2–4 were obtained following reported methodologies;<sup>6–8</sup> spectroscopic data are in good agreement.

**Instrumentation.** NMR spectra were recorded on Jeol ECA 500 and Jeol 270 MHz spectrometers using deuterated solvents; chemical shifts for <sup>1</sup>H and <sup>13</sup>C NMR data are relative to the residual nondeuterated solvent signal, fixed at  $\delta = 7.26$  ppm for <sup>1</sup>H NMR and  $\delta = 77.00$  ppm for <sup>13</sup>C NMR. Infrared spectra were registered on an FT-IR Varian ATR spectrometer. HRMS data were acquired using an Agilent G1969A MS TOF spectrometer. Elemental analysis for MR2 was determined on a Thermofinnigan Flash 1112 equipment (CHONS). Absorption spectra were obtained in chloroform solutions using a PerkinElmer Lambda 2S UV/vis spectrophotometer.

**2.2. Synthetic Procedures. Synthesis of Molecular Rotors. 2,5-Bis((9,9-dioctyl-fluorene-2-yl)ethynyl)pyridine (MR1).** 2-Ethynyl-9,9-dioctylfluorene (**4**) (0.20 g, 0.48 mmol), 2,5-dibromopyridine (**5**) (0.06 g, 0.25 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 g, 0.028 mmol), and CuI (0.009 g, 0.03 mmol) were placed in a dried round-bottom flask, followed by the addition of diisopropylamine (1 mL) and freshly distilled THF (25 mL) under a nitrogen atmosphere. The mixture was refluxed 8 h, allowed to cool to room temperature, quenched with a saturated solution of ammonium chloride (25 mL), extracted with ethyl acetate (3 × 25 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated to dryness, and chromatographed on silica gel (70–230 Mesh) using hexanes. The brown solid thus obtained was recrystallized from deuterated chloroform and acetonitrile to yield 80 mg (37%) of MR1 as a yellow solid. M.P. 78–79 °C. FTIR (ATR cm<sup>-1</sup>):  $\nu$  3268, 2923, 2875, 2316,

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