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. These crystal systems, expected to display interesting properties like dichroism and birefringence, 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. 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-diocetylfluorene groups as stators and pyridine and fluorobenzene rings as polar rotators. The static dipolar moments present in 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.

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; 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 1H and 13C NMR data are relative to the residual nondeuterated solvent signal, fixed at δ = 7.26 ppm for 1H NMR and δ = 77.00 ppm for 13C 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-diocetyl-fluorene-2-y1)ethynyl)pyridine (MR1). 2-Ethynyl-9,9-diocetylfluorene (4) (0.20 g, 0.48 mmol), 2,5-dibromopyridine (5) (0.06 g, 0.25 mmol), Pd(PPh3)4 (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) using hexanes. 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 Na2SO4, 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⁻¹): ν 3268, 2923, 2875, 2316, …