

Article



Subscriber access provided by Weizmann Institute of Science

# Synthesis of a carbazole-[pi]-carbazole molecular rotor with fast solid state intramolecular dynamics and crystallization-induced emission

Andres Aguilar-Granda, Salvador Perez-Estrada, Arián E. Roa, Joelis Rodriguez-Hernandez, Simón Hernandez-Ortega, Mario Rodriguez, and Braulio Rodríguez-Molina

Cryst. Growth Des., Just Accepted Manuscript • DOI: 10.1021/acs.cgd.6b00395 • Publication Date (Web): 19 Apr 2016 Downloaded from http://pubs.acs.org on April 21, 2016

# **Just Accepted**

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



Crystal Growth & Design is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

#### 

# Synthesis of a carbazole-[pi]-carbazole molecular rotor with fast solid state intramolecular dynamics and crystallization-induced emission.

Andrés Aguilar-Granda,<sup>a</sup> Salvador Pérez-Estrada,<sup>b</sup> Arian E. Roa,<sup>c</sup> Joelis Rodríguez-Hernández,<sup>d</sup> Simón Hernández-Ortega,<sup>a</sup> Mario Rodriguez,<sup>c</sup> and Braulio Rodríguez-Molina.<sup>a</sup>\*

<sup>*a*</sup>Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Ciudad de México, 04510, México.

<sup>b</sup>Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States.

<sup>c</sup>Centro de Investigaciones en Óptica, A.P. 1-948, León, Guanajuato, 37000, México

<sup>*d*</sup>Centro de Investigación en Química Aplicada (CIQA), Blvd. Enrique Reyna Hermosillo No. 140, Saltillo, Coahuila, 25294, México.

Corresponding author: \*brodriguez@iquimica.unam.mx.

# Abstract

Herein we report the synthesis of the highly stable crystalline carbazole-based rotor **3** with simultaneous rapid solid state internal rotation and good fluorescence emission. Single crystal and powder X-ray diffraction studies along with microscopy revealed a phase transition from a labile benzene solvate (phase I) to highly stable crystals (phase II) that feature fast intramolecular rotation in the megahertz regime at room temperature, according with VT 2H solid state NMR experiments using isotopically enriched analogs. In addition to the megahertz rotation within its crystals, this crystal phase II displays enhanced solid state fluorescence with a higher quantum yield of  $\phi = 0.28$ , relative to the emission of this compound in THF solution ( $\phi = 0.06$ ). These two solid state properties are significantly different to shorter compounds 1 and 2 (static and non-emissive) included here for comparison purposes.



# Synthesis of a carbazole-[pi]-carbazole molecular rotor with fast solid state intramolecular dynamics and crystallization-induced emission.

Andrés Aguilar-Granda,<sup>a</sup> Salvador Pérez-Estrada,<sup>b</sup> Arian E. Roa,<sup>c</sup> Joelis Rodríguez-Hernández,<sup>d</sup> Simón Hernández-Ortega,<sup>a</sup> Mario Rodriguez,<sup>c</sup> and Braulio Rodríguez-Molina.<sup>a</sup>\*

<sup>*a*</sup>Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Ciudad de México, 04510, México.

<sup>b</sup>Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States.

<sup>c</sup>Centro de Investigaciones en Óptica, A.P. 1-948, León, Guanajuato, 37000, México

<sup>d</sup>Centro de Investigación en Química Aplicada (CIQA), Blvd. Enrique Reyna Hermosillo No. 140, Saltillo, Coahuila, 25294, México.

# Abstract

Herein we report the synthesis of the highly stable crystalline carbazole-based rotor **3** with simultaneous rapid solid state internal rotation and good fluorescence emission. Single crystal and powder X-ray diffraction studies along with microscopy revealed a phase transition from a labile benzene solvate (phase **I**) to highly stable crystals (phase **II**) that feature fast

#### **Crystal Growth & Design**

intramolecular rotation in the megahertz regime at room temperature, according with VT <sup>2</sup>H solid state NMR experiments using isotopically enriched analogs. In addition to the megahertz rotation within its crystals, this crystal phase **II** displays enhanced solid state fluorescence with a higher quantum yield of  $\phi$ = 0.28, relative to the emission of this compound in THF solution ( $\phi$ = 0.06). These two solid state properties are significantly different to shorter compounds **1** and **2** (static and non-emissive) included here for comparison purposes.

#### Introduction

Biomolecular machines found in Nature represent extremely refined examples of how multiple molecular motions can collectively translate into complex functions; for example, the conformational changes occurring in proteins that define their specific activity.<sup>1</sup> A great effort has been devoted to design compounds that can be regarded as synthetic molecular machines as they emulate the functions of their natural counterparts.<sup>2-4</sup> In some cases, the intended function is the result of combined molecular motion (rotation) that modify the mechanical or optical properties of a material,<sup>5</sup> or large structural changes that change the conjugation and thus the absorption and emission of the compounds (fluorescence),<sup>6</sup> among other properties that can be modulated for the development of responsive materials.<sup>7-10</sup> Other functional materials with externally controllable properties, e.g. nonlinear optics or electric conductivity have been envisioned to arise also from the control of the molecular rotation, giving rise to the field of molecular rotors, molecular machines that feature a highly mobile molecular fragment attached to static components.<sup>11</sup>

In this context, it is clear that both molecular rotation and fluorescence are exciting properties that should be interesting to combine in organic solids. In order to develop such new compounds, it is worth to consider the Aggregation-Induced Emission phenomenon (AIE),<sup>12-14</sup> in which fast

rotation of the molecular components *in solution* produces non-emissive solutions. Conversely, these AIE compounds render highly fluorescent solids attributed to the restricted rotation upon crystallization. Similarly, some weakly emitting compounds in solution show enhanced fluorescence when they form aggregates, a property that has been described as Crystallization-Induced Emission or Aggregation-Induced Enhanced Emission (CIE and AIEE, respectively), again as a result of the restriction of the intramolecular rotations.<sup>15-18</sup> However, to the best of our knowledge, information about the precise frequency of the resulting motion in the solid state, or the lack of it, is still limited.<sup>19-21</sup>

On the other side, systematic studies of the nature and frequency of the molecular rotation in crystals have been carried out in the already mentioned field of the molecular rotors. Very important contributions highlighting the structural requirements that promote fast molecular motion in solids have been reported by the groups of Michl,<sup>22-24</sup> Sozzani,<sup>25,26</sup> Garcia-Garibay<sup>27-29</sup> and Batail<sup>30,31</sup> among others.<sup>32-37</sup> In those previous works, it has been described that the rotating component (*rotator*) should be attached to an *axis* that imposes low rotational friction and this resulting fragment should be effectively protected from intermolecular interactions by a voluminous framework (*stator*) in order to reach high rotational frequencies. Importantly, solid state emission has been scarcely reported in crystalline molecular rotors,<sup>38</sup> perhaps due to the low extent of conjugation of the resulting molecules.



Figure 1. Compounds **1-3** showing the possible intramolecular effects that restrict rotation. The elongation of the molecular axis frees their internal motion in crystals (double headed arrow).

In this work, we have focused in the synthesis and solid state characterization of an initial series of symmetrical, conjugated carbazole-[pi]-carbazole compounds **1-3**, adapting some of the elements from the molecular rotors blueprints for intramolecular dynamics and using an architecture that enhances the electrodonating property of the carbazole for emission purposes,<sup>39</sup> similar to those that have been previously employed in organic light-emitting diodes (OLEDs).<sup>40-45</sup> This heterocycle was also chosen given its modifiable structure<sup>46,47</sup> and because it represents an equilibrium between a thermally stable compound, has a great ability to form edge to face interactions in the solid state and is medium size stator that could enable intramolecular motion. We intended to facilitate their internal rotation and to increase their emission properties by extending the conjugation producing linear structures as illustrated in Figure 1. Interestingly, when the 1,4-diethynylphenylene fragment is bound to two 9-phenylcarbazole units in compound **3**, rotation in the fast exchange regime is attained as evidenced by detailed solid state <sup>2</sup>H NMR,

calorimetric and X-ray diffraction studies. In addition to the precise nature of the internal rotation, this work describes the enhanced fluorescence of compound **3** in its crystalline form when compared to its emission in THF solution, as indicated by photoluminescence experiments described below.

#### Experimental

All reagents were purchased from Sigma-Aldrich and used as received. THF was dried prior to use by distillation (Na/benzophenone). Flash column chromatography and flash chromatography were performed with Sigma-Aldrich silica gel (230-400 mesh), unless otherwise stated. Reactions were monitored by TLC on silica gel plates 60 F<sub>254</sub> and the spots were detected by a combination of UV/Seebach's stain. Inert atmosphere reactions were carried out under nitrogen. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at ambient temperature using Bruker Fourier 300, Jeol Eclipse 300, Bruker Avance, Bruker Avance500 with Cryoprobe spectrometers and referenced to TMS (0.0 ppm) and CDCl<sub>3</sub> (77.0 ppm) respectively, unless otherwise noted. The FT-IR spectral data were recorded in a Bruker ATR in the 450-4000 cm<sup>-1</sup> range. Uncorrected melting points were determined in a Fisher Johns melting point apparatus. HRMS were obtained by Direct Analysis in Real Time (DART) or by Fast Atom Bombardment (FAB<sup>+</sup>) in a MStation, JMS-700 spectrometer.

*Bis(carbazol-9-yl)phenylene* (1). In a two neck round-bottom flask a mixture of carbazole (0.500 g, 2.99 mmol), 1,4-diiodobenzene (0.493 g, 1.49 mmol), CuI (0.028 g, 0.14 mmol), 18-crown-6 (0.013 g, 0.04 mmol), K<sub>2</sub>CO<sub>3</sub> (0.826 g, 5.97 mmol) and *N,N'*-Dimethylpropylene urea (3 mL) was heated to 140 °C and stirred for 1 h under nitrogen atmosphere. The mixture was cooled to room temperature then added 40 mL of saturated solution of NH<sub>4</sub>Cl and extracted with dichloromethane (3x30 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the

Page 7 of 32

#### **Crystal Growth & Design**

solvent was removed under vacuum. The resulting residue was precipitated (from what solvent) using acetonitrile to give a beige solid (1.0992g, 90%, M. P. by DSC 322-324 °C). The solid was recrystallized twice from dichloromethane/ethyl acetate (1:1) to afford colorless crystals. IR  $v_{max}$ : 3051, 1592, 1513, 1444, 1311, 1224, 748, 720 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.2 (d, 4H,  ${}^{3}J=$  7.8 Hz), 7.8 (s, 4H), 7.6 (d, 4H,  ${}^{3}J=$  8.2 Hz), 7.5 (m, 4H), 7.4 (m, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.8 (C9a), 136.7 (C10), 128.4 (C11), 126.2 (C2), 123.6 (C4a), 120.4 (C4), 120.3 (3), 109.8 (C1). HMRS (DART) m/z [C<sub>30</sub>H<sub>21</sub>N<sub>2</sub>]<sup>+</sup> calcd. 409.1704, found 409.1703.

*Bis(carbazol-9-yl)phenylene-d*<sub>4</sub> (**1-***d*<sub>4</sub>). The same procedure for **1** was used to prepare **1**-*d*<sub>4</sub> using the following amounts: carbazole (0.500 g, 2.99 mmol), 1,4-diiodobenzene-*d*<sub>4</sub> (0.458 g, 1.49 mmol), CuI (0.028 g, 0.14 mmol), 18-crown-6 (0.013 g, 0.04 mmol), K<sub>2</sub>CO<sub>3</sub> (0.826 g, 5.97 mmol) and N,N'-Dimethylpropylene urea (3 mL) was heated to 140 °C and stirred for 1 h under nitrogen atmosphere according with the previous methodology. The resulting product was beige (1.099g, 90%, M. P. by DSC 322-324 °C). IR v<sub>max</sub>: 3050, 1592, 1445, 1309, 1225, 748, 720 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.21 (d, 4H, <sup>3</sup>*J*= 7.8 Hz), 7.59 (d, 4H, <sup>3</sup>*J*= 8.21 Hz), 7.49 (m, 4H), 7.36 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.8 (C9a), 136.7 (C10), 128.4 (C11), 126.2 (C2), 123.6 (C4a), 120.4 (C4), 120.3 (3), 109.8 (C1). HMRS (DART) *m/z* [C<sub>30</sub>H<sub>17</sub>H<sub>4</sub>N<sub>2</sub>]<sup>+</sup> calcd. 413.19558, found 413.19551.

*1,2-bis(4-(9H-carbazol-9-yl)phenyl)ethyne* (**2**). In a two-neck round-bottom flask a mixture of N-(4-ethynylphenyl)carbazole (**6**) (0.500 g, 1.87 mmol), N-(4-Iodophenyl)carbazole (**4**) (0.690 g, 1.87 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.131, 0.187 mmol), CuI (0.017 g, 0.089 mmol), dry THF (6 mL) and 1 mL of triethylamine was stirred for 2 h at room temperature under nitrogen atmosphere, then the mixture was washed with 30 mL of a saturated solution of NH<sub>4</sub>Cl and the organic phase was extracted with dichloromethane (3x30 mL). The combined organic layers were dried over

Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed by evaporation. The resulting product was precipitated from dichloromethane using acetonitrile to give a yellow solid (0.626 g, 70%, M. P. by DSC 308-310 °C). IR  $v_{max}$ : 3052, 1598, 1516, 1447, 1336, 1223, 833, 748 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.2 (d, 4H, <sup>3</sup>*J*= 7.8 Hz), 7.8 (d, 4H, <sup>3</sup>*J*= 8.26 Hz), 7.6 (d, 4H, <sup>3</sup>*J*= 8.3 Hz), 7.5 (m, 4H), 7.3 (m, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.6 (C9a), 137.9 (C10), 133.3 (C12), 127.0 (C11), 126.2 (C2), 123.7 (C4a), 122.0 (C13), 120.5 (C4), 120.4 (C3), 109.8 (C1), 89.7 (C14). HMRS (FAB) calcd for *m/z* [C<sub>38</sub>H<sub>24</sub>N<sub>2</sub>]<sup>+</sup> calcd. 508.1939, found 508.1944.

*1,2-bis(4-(9H-carbazol-9-yl)phenyl)ethyne-d*<sub>8</sub> (**2-** *d*<sub>8</sub>). The same procedure for compound **2** was used to prepare **2-***d*<sub>8</sub> with the following amounts: N-(4-ethynylphenyl)carbazole-*d*<sub>4</sub> (**6-***d*<sub>4</sub>). (0.500 g, 1.84 mmol), N-(4-Iodophenyl)carbazole-*d*<sub>4</sub> (**4-***d*<sub>4</sub>) (0.687 g, 1.84 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.129 g, 0.184 mmol), CuI (0.017 g, 0.092 mmol), dry THF (6 mL) and triethylamine (1mL) was stirred by 2 h at room temperature under nitrogen atmosphere according to the previous methodology. The resulting product was precipitated dichloromethane using using acetonitrile to give a yellow solid (0.627g, 70%, M. P. by DSC 308-310 °C). IR v<sub>max</sub>: 3042, 1593, 1554, 1449, 1319, 1226, 991, 745, 422 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.2 (d, 4H, <sup>3</sup>*J*= 7.7 Hz), 7.5 (m, 4H), 7.3 (m, 4H9). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.6 (C9a), 137.8 (C10), 126.2 (C2), 123.7 (C4a), 121.9 (C13), 120.5 (C4), 120.3 (C3), 109.9 (C1), 89.5 (C14). HMRS (DART) *m/z* [C<sub>38</sub>H<sub>17</sub><sup>2</sup>H<sub>8</sub>N<sub>2</sub>]<sup>+</sup> calcd. 517.25199, found 517.25233.

*1, 4-bis(9H-carbazol-9-yl)phenyl)ethynyl)benzene* (**3**). Under nitrogen atmosphere in a two neck round-bottom flask a mixture of N-(4-ethynylphenyl)carbazole (**6**) (0.500 g, 1.85 mmol), 1,4 diiodobenzene (0.306 g, 0.92 mmol),  $PdCl_2(PPh_3)_2$  (0.130 g, 0.185 mmol), CuI (0.017 g, 0.08 mmol), dry THF (6 mL) and 1 mL of triethylamine was stirred by 2 h at room temperature, then to the mixture was added 30 mL of a saturated solution of NH<sub>4</sub>Cl and the organic phase was

extracted with dichloromethane (3x30 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was reduced by evaporation. The desired compound was precipitated from dichloromethane using acetonitrile to give an orange solid (0.398g, 70%, M. P. by DSC 303-305 °C). IR  $\nu_{max}$ : 3038, 1593, 1513, 1448, 1332, 1222, 835, 720 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.2 (d, 4H, <sup>3</sup>*J*= 7.8 Hz), 7.8 (d, 4H, <sup>3</sup>*J*= 8.6 Hz), 7.6 (d, 4H, <sup>3</sup>*J*= 8.5 Hz), 7.6 (s, 4H), 7.4 (m, 4H), 7.3 (m, 4H). 7.3 (m, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.5 (C9a), 137.5 (C10), 133.2 (C12), 131.7 (C17), 126.9 (C11), 126.1 (C2), 123.6 (C4a), 123.1 (C16), 122.0 (C13) 120.4 (C4), 120.3 (3), 109.8 (C1), 90.7 (C14), 90.0 (C15). HMRS (FAB) m/z [C<sub>46</sub>H<sub>28</sub>N<sub>2</sub>]<sup>+</sup> calcd. 608.2252, found 608.2248.

*1*, 4-*bis(9H-carbazol-9-yl)phenyl)ethynyl)benzene-d*<sup>8</sup> (**3**-*d*<sup>8</sup>). The same procedure for compound **3** was used to prepare **3**-*d*<sup>8</sup> using the following amounts: N-(4-ethynylphenyl)carbazole-d<sub>4</sub> (**6**-*d*<sub>4</sub>). (0.500 g, 1.84 mmol), 1,4-diiodobenzene (0.303 g, 0.92 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.129, 0.184 mmol), CuI (0.017 g, 0.092 mmol), dry THF (6 mL) and triethylamine (1mL) was stirred by 2 h at room temperature under nitrogen atmosphere. The resulting product was an orange solid (0.391g, 69%, M. P. by DSC 303-305 °C). IR v<sub>max</sub>: 3040, 1573, 1451, 1307, 1222, 1009, 873, 739, 647 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.2 (d, 4H, <sup>3</sup>*J*= 7.8), 7.6 (s, 4H), 7.4 (m, 4H,) 7.3 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.5 (C9a), 137.7 (C10), 132.9 (C12, *J*<sub>C-D</sub>= 24.05 Hz), 131.7 (C17), 126.5 (C11, *J*<sub>C-D</sub>= 24.05 Hz), 126.1 (C2), 123.6 (C4a), 123.1 (C16), 121.7 (C13), 120.4 (C4), 120.3 (3), 109.8 (C1), 90.6 (C14), 90.0 (C15). HMRS (DART) *m*/z [C<sub>46</sub>H<sub>21</sub><sup>2</sup>H<sub>8</sub>N<sub>2</sub>]<sup>+</sup> calcd. 617.28329, found 617.28100.

*1, 4-bis(9H-carbazol-9-yl)phenyl)ethynyl)benzene-d*<sub>4</sub> (**3-d**<sub>4</sub>). The same procedure for compound **3** was used to prepare **3-d**<sub>4</sub> using the following amounts: N-(4-ethynylphenyl)carbazole-d<sub>4</sub> (**6**) (0.500 g, 1.80 mmol), 1,4-diiodobenzene-d<sub>4</sub> (0.302 g, 0.90

#### **ACS Paragon Plus Environment**

mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.127 g, 0.180 mmol), CuI (0.017 g, 0.090 mmol), dry THF (6 mL) and triethylamine (1mL) was stirred for 2 h at room temperature under nitrogen atmosphere. The resulting product was an orange solid (0.391g, 69%, M. P. by DSC 303-305 °C). IR v<sub>max</sub>: 3044, 1597, 1512, 1448, 1314, 1223, 1001, 834, 718 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.2 (d, 4H,  ${}^{3}J=7.7$  Hz), 7.8 (d, 4H,  ${}^{3}J=8.6$  Hz), 7.6 (d, 4H,  ${}^{3}J=8.6$ Hz), 7.4 (m, 4H,) 7.3 (m, 4H).  ${}^{13}C$  NMR (75 MHz, CDCl<sub>3</sub>) δ: 140.5 (C9a), 137.8 (C10), 133.1 (C12), 131.3 (C17, J<sub>C-D</sub>=25.4 Hz), 126.8 (C11), 126.1 (C2), 123.6 (C4a), 122.9 (C16), 121.9 (C13), 120.4 (C4), 120.3 (3), 109.8 (C1), 90.7 (C14), 90.0 (C15). HMRS (DART)  $m/z [C_{46}H_{25}^{2}H_4N_2]^+$  calcd. 613.25818, found 613.25770. N-(4-Iodophenyl)carbazole (4). In a two-neck round-bottom flask a mixture of carbazole (0.500 g, 2.99 mmol), 1,4-diiodobenzene (1.97 g, 5.98 mmol), CuI (0.028 g, 0.14 mmol), 18-crown-6 (0.013 g, 0.04 mmol), K<sub>2</sub>CO<sub>3</sub> (0.826 g, 5.97 mmol) and N,N'-Dimethylpropylene urea (6 mL) was heated to 140 °C and stirred for 1 h under nitrogen atmosphere. After cooling to room temperature, the mixture was quenched with water and the resulting precipitate was filtered. The resulting solid was dissolved in dichloromethane then washed with 40 mL of saturated solution of  $NH_4Cl$  and the aqueous layer was further extracted with dichloromethane (3x30 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed by evaporation. The resulting residue was purified by column chromatography (100% hexanes) to afford compound 4 as a white solid (0.993 g, 90%, M. P. 139-141 °C). IR v<sub>max</sub>: 3054, 1578, 1479, 1447, 1338, 1001, 821, 746, 566 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.2 (d, 1H, <sup>3</sup>J= 7.7 Hz), 7.9 (d, 1H,  ${}^{3}J=$  7.7 Hz), 7.4 (m, 2H), 7.3 (m, 3H).  ${}^{13}C$  NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.6 (C9a), 139.2 (C12), 137.7 (C10), 129.0 (C11), 126.2 (C2), 123.6 (C4a), 120.5 (C4), 120.4 (C3), 109.7 (C1), 92.1 (C13). HMRS (DART)  $m/z [C_{18}H_{13}NI]^+$  calcd. 370.0092, found 370.0101.

#### **Crystal Growth & Design**

*N-(4-Iodophenyl)carbazole-d*<sub>4</sub> (**4-***d*<sub>4</sub>). The same procedure for compound **1** was used to prepare **4-***d*<sub>4</sub> with the following amounts: carbazole (0.500 g, 2.99 mmol), 1,4-diiodobenzene (1.99 g, 5.98 mmol), CuI (0.028 g, 0.14 mmol), 18-crown-6 (0.013 g, 0.04 mmol), K<sub>2</sub>CO<sub>3</sub> (0.826 g, 5.97 mmol) and N,N'-Dimethylpropylene urea (6 mL) was heated to 140 °C and stirred for 1 h under nitrogen atmosphere. Compound **4-***d*<sub>4</sub> was obtained as a white solid (0.993 g, 90%, M. P. 139-141 °C). IR v<sub>max</sub> 3041, 1552, 1449, 1404, 1334, 1227, 991, 746, 628 563 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.2 (d, 1H, <sup>3</sup>*J*= 6.8 Hz), 7.4 (m, 2H), 7.3 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.6 (C9a), 138.7 (C12, *J*<sub>C-D</sub>= 25.5 Hz), 137.7 (C10), 128.4 (C11, *J*<sub>C-D</sub>= 25.5 Hz), 126 (C2), 123.4 (C4a), 120.3 (C4), 120.2 (C3), 109.5 (C1), 91.6 (C13). HMRS (DART) *m/z* [C<sub>18</sub>H<sub>9</sub><sup>2</sup>H<sub>4</sub>N<sub>1</sub>]<sup>-</sup> /<sup>+?</sup> calcd. 374.03437, found 374.03462.

*N-(4-trimethylsilylethynylphenyl)carbazole* (5). To a two-neck round-bottom flask was added N-(4-todophenyl)carbazole (4) (0.500 g, 1.35 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.95 g, 0.135 mmol), CuI (0.012 g, 0.067 mmol), ethynyltrimethylsilane (0.132 g, 1.35 mmol), dry THF (6 mL) and triethylamine (1 mL) under nitrogen atmosphere. The reaction mixture was stirred for 2 h at room temperature then added 30 mL of saturated solution of NH<sub>4</sub>Cl and extracted with dichloromethane (3x30 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuum. The crude product was purified by column chromatography (100% hexanes) to afford compound **5** as a yellow solid (0.461 g, 95%, M. P. 158-160 °C). IR  $v_{max}$ : 3053, 2957, 2157, 15985, 1507, 1224, 839 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.1 (d, 2H, <sup>3</sup>*J*= 7.8 Hz), 7.7 (d, 2H, <sup>3</sup>*J*= 8.2 Hz), 7.5 (d, 4H, <sup>3</sup>*J*= 8.7 Hz), 7.4 (m, 4H), 7.3 (m, 3H), 0.3 (s, 9) <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.6 (C9a), 137.9 (C10), 133.7 (C12), 126.8 (C11), 126.1 (C2), 123.6 (C4a), 122.2 (C13), 120.5 (C4), 120.3 (C3), 109.7 (C1), 104.4 (C15), 95.5 (C14), 0.30 (C16). HMRS (DART) *m/z* [C<sub>23</sub>H<sub>22</sub>N<sub>1</sub>Si<sub>1</sub>]<sup>+</sup> calcd. 340.1521, found 340.1510.

*N-(4-trimethylsilylethynylphenyl)carbazole-d*<sub>4</sub> (**5-***d*<sub>4</sub>). A degased mixture of N-(4iodophenyl)carbazole-d<sub>4</sub> (**4-***d*<sub>4</sub>) (0.500 g, 1.35 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.95 g, 0.135 mmol), CuI (0.012 g, 0.067 mmol), dry THF (6 mL), ethynyltrimethylsilane (0.132 g, 1.35 mmol) and triethylamine (1 mL) was stirred for 2 h at room temperature. The reaction mixture was treated with 30 mL of a saturated solution of NH<sub>4</sub>Cl, then extracted with dichloromethane (3x30 mL); the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness under vacuum. The crude product was purified by column chromatography (100% hexanes) to afford compound **5-***d*<sub>4</sub> as a yellow solid (0.460g, 95%, M. P. 158-160 °C). IR v<sub>max</sub>: 2925, 1611, 1511, 1243, 1040, 726, 686 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.2 (d, 2H, <sup>3</sup>*J*= 7.7 Hz), 7.4 (m, 4H), 7.3 (m, 2H), 0.3 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.5 (C9a), 137.6 (C10), 126.0 (C2), 123.6 (C4a), 120.3 (C4), 120.2 (C3), 109.7 (C1), 104.2 (C15), 95.4 (C14), 0.05 (C16). HMRS (DART) *m/z* [C<sub>23</sub>H<sub>18</sub><sup>2</sup>H<sub>4</sub>N<sub>1</sub>Si<sub>1</sub>]<sup>+</sup> calcd. 344.17726, found 344.17703.

*N-(4-ethynylphenyl)carbazole* (6). A solution of N-(4-trimethylsilylethynylphenyl)carbazole (5) (0.500 g, 1.47 mmol) in dry THF (6 mL) was treated with tetrabutylammonium fluoride 2.5M in THF (0.385 g, 1.47 mmol). The reaction mixture was stirred at room temperature under nitrogen atmosphere for 2 h to then quench with saturated solution of NH<sub>4</sub>Cl (30 mL). The organics were extracted with dichloromethane (3x30 mL), then the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed by evaporation. The resulting residue was purified by column chromatography (100% hexanes) to afford compound **6** as a white solid (0.374 g, 95%, M. P.103-104 °C). IR v<sub>max</sub>: 3258, 1597, 1446, 1332, 1222, 749 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.2 (d, 2H, <sup>3</sup>*J*= 7.8 Hz), 7.7 (d, 2H, <sup>3</sup>*J*= 8.7 Hz), 7.6 (d, 2H, <sup>3</sup>*J*= 8.5 Hz), 7.4 (m, 4H), 7.3 (m, 2H), 3.2 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.6 (C9a), 138.2 (C10),

#### **Crystal Growth & Design**

133.8 (C13), 126.9 (C12), 126.2 (C2), 123.7 (C4a), 121.2 (C11), 120.5 (C4), 120.3 (C3), 109.8 (C1), 83.0 (C14), 78.2 (C15). HMRS (DART)  $m/z [C_{20}H_{14}N]^+$  calcd. 268.1126, found 268.1124.  $N-(4-ethynylphenyl)carbazole-d_4$  $(6-d_4)$ . А of N-(4solution trimethylsilylethynylphenyl)carbazole- $d_4$  (5- $d_4$ ) (0.500 g, 1.45 mmol) in dry THF (6 mL) was treated with tetrabutylammonium fluoride 2.5M in THF (0.380 g, 1.45 mmol). The reaction mixture was stirred at room temperature under nitrogen atmosphere for 2 h, then quenched with saturated solution of  $NH_4Cl$  (30 mL) and extracted with dichloromethane (3x30 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed by evaporation. The crude product was purified by column chromatography (100% hexanes) to provide compound **6-d**<sub>4</sub> as a white solid (0.375 g, 95%, M. P.103-104 °C). IR v<sub>max</sub>: 3259, 3043, 2166, 1687, 1595, 1448, 1222, 834, 718 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.2 (d, 2H, <sup>3</sup>J= 7.75 Hz), 7.5 (m, 2), 7.3 (m, 1H) 3.2 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 140.5 (C9a), 138. (C10), 133.2  $(C12, J_{C-D}=25.3 \text{ Hz}), 126 (C2), 123.6 (C4a), 120.4 (C4), 120.3 (C3), 109.7 (C1), 82.9 (C14), 120.3 (C3), 109.7 (C1), 1$ 78.2 (C15). HMRS (DART) m/z  $[C_{20}H_{10}^{2}H_{4}N]^{+}$  calcd. 272.13773, found 272.13765.

# **Results and discussion.**

Synthesis and characterization. Natural abundance compounds 1 and 2 have been reported by others,<sup>48-50</sup> but studies of their potential internal dynamics have not been performed and samples were synthesized to fully characterize them in the solid state and contrast their properties with the novel molecular rotor 3 obtained in 57 % yield over four steps. In addition, we also synthesized isotopically enriched derivatives  $1-d_4$ ,  $2-d_8$ ,  $3-d_8$ , and  $3-d_4$  with deuterated inner phenylenes to probe chemical exchange processes in the MHz regime as detailed in the following sections. Natural abundance and isotopic analogs were obtained in good yields following the synthetic route in Scheme 1, where 1,4-diiodobenzene or a homemade 1,4-

diiodobenzene- $d_4$  was covalently linked to the carbazol units through Ullman-type reactions. Subsequently, the extended conjugation was achieved by means of Pd(0)-catalyzed Sonogashira reactions. Detailed spectroscopic characterization of all compounds is included in the *Supporting Information*.

Scheme 1. Synthesis of deuterium enriched derivatives  $1-d_4$ ,  $2-d_8$ ,  $3-d_8$ , and  $3-d_4$ 



# Single crystal X-ray diffraction studies

Crystals of compound 1 were grown as described previously in reference 49 but the crystal structure was determined now at 295 K to better match the structural details with the photophysics of the material which was also determined at room temperature. Crystals of compound 2 were grown from slow evaporation of THF and solved in the space group  $P2_1/c$ . In the case of molecular rotor 3, its considerably low solubility only allowed to grow a benzene solvate (labeled phase I) which was collected at 150 K and solved in the space group C2/c (Figure 2). Additionally, a second solvent-free phase of compound 3, labeled as phase II, was

grown either from THF or from dichloromethane as small needles that were unsuitable for single crystal X-ray diffraction experiments but with cell constants a = 9.774(1), b = 11.392(2) and c = 14.541(2) and angles alpha = 100.729(9), beta = 90.633(10) and gamma = 95.057(10), that perfectly match with those obtained from the powder X-ray diffraction pattern<sup>51</sup> with cell constants a = 9.778(2), b = 11.404(1), c = 14.568(3) and angles alpha= 100.83(2), beta= 90.64(3) and gamma= 95.27(2). The relevant crystallographic parameters of compounds 1-3 are compiled in Table 1.



Figure 2. ORTEP structures of (a) compound 1, (b) compound 2 and (c) compound 3 as a benzene solvate.

A detailed inspection of compound **1** showed a highly twisted structure where each component laid in different planes resulting in an array with one molecule per asymmetric unit (Z'=1). In compound **2**, the two internal phenyl rings are virtually coplanar, but the molecule adopts a curved shape due to the carbazole units with perpendicular conformations, also resulting with one molecule per asymmetric unit (Z'=1). In both compounds, the phenyl rings attached to the carbazole experience a highly crowded environment from their neighboring molecules that could affect their potential dynamics (see *Supporting Information*).



Figure 3. Crystal packing of the solvate of compound **3**, down the *b*-axis with the entrapped benzene molecules (highlighted in purple) in between the elongated molecules.

In the case of the benzene solvate of compound **3** illustrated in Figure 3, the three phenylene rings adopt a fully coplanar conformation making a dihedral angle with respect to the carbazoles of ca. 61°. Although the heterocycles laid in different planes, the asymmetric unit is only half a molecule (Z'=0.5), resulting from an inversion point that coincides with the centroid of the central phenyl ring. The crystal packing of **3** indicates a ladder array of molecules with encapsulated benzene rings in between neighboring molecular rotors showing an edge-to-face interaction with a CH<sub>benzene</sub>-centroid distance of 2.72 Å and an angle of 152°.

Table 1. Relevant crystallographic parameters of compounds 1-3.

	Compound $1^{a}$	Compound 2	Compound <b>3</b> (benzene solvate)
Formula	$C_{30}H_{20}N_2$	$C_{38}H_{24}N_2$	$C_{64}H_{46}N_2$
$MW/g mol^{-1}$	408.48	508.59	843.03
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbca	$P2_1/c$	C2/c
a/Å	8.195 (5)	5.4678 (10)	18.7320 (5)
b/Å	16.533 (12)	34.8288 (10)	5.7487 (2)
c/Å	32.070 (2)	14.1542 (4)	44.4908 (14)

# Crystal Growth & Design

1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	
13	
14	
15	
16	
17	
18	
19	
20	
21	
22	
23	
24	
25	
26	
27	
28	
29	
30	
31	
32	
33	
34	
35	
36	
37	
38	
39	
40	
41	
42	
43	
44	
45	
46	
47	
48	
49	
50	
51	
52	
53	
54	
55	
56	
57	
58	
59	
60	
111	

α(°)	90	90	90	
β(°)	90	97.28	99.890 (2) 90	
γ(°)	90	90		
$V/Å^3$	4345.3 (5)	2673.7(1)	4719.8(3)	
Ζ	8	4	4	
Z'	1	1	0.5	
$\rho c/g \ cm^{-3}$	1.249	1.263	1.186	
Collected Refl.	3958	21222	18240	
Ind. Ref. (Rint)	3958	4890	4277	
$R[F^2 > 2\sigma(F^2)]$	0.073	0.0536	0.0474	
R <sub>w</sub> (all data)	0.1604	0.1521	0.1194	
$\Delta \rho_{max}/e \ \text{\AA}^3$	0.25	0.137	0.229	
$\Delta \rho_{min}/e \text{ Å}^3$	-0.19	-0.198	-0.211	
Т	298 (2)	296 (2)	150 (2)	

<sup>a</sup>Similar parameters to those reported in ref.49

# Thermal stability experiments.



Figure 4. Optical micrographs of the benzene solvate of **3** taken every 30 minutes at room temperature.

Immediately after the X-ray diffraction experiments, it was noted that benzene solvate crystals of **3** became opaque and the powder X-ray diffraction pattern of the resulting solid was in excellent agreement with those obtained from crystals grown from THF or dichloromethane. In order to obtain a timescale of this phase transition, freshly grown crystals of **3** from benzene were monitored under an optical microscope at room temperature. As illustrated in Figure 4, the solvate crystals fractured under illumination and lost their prime quality in less than two hours, reflecting that the benzene is loosely bound. Given this information, we decided to further explore the thermal stabilities of all compounds by differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) looking for less evident phase transitions. Crystalline samples of compounds 1 and 2, verified by powder X-ray diffraction analyses, showed only endothermic peaks in their DSC traces attributed to their melting points at 322-324 °C and 302-310 °C, respectively. Their TGA analyses indicated subtle losses of weight that were considered as residual solvent of crystallization that did not affected their known crystal array. In the case of molecular rotor **3**, only the desolvated form was analyzed showing high thermal stability with a melting point of 300-305 °C. As noted, slightly lower melting points were observed in compounds 1-3 as their molecular axis is larger, but no additional phases were discovered.

#### Solid state NMR CPMAS analyses

Initial characterization by means of solid state <sup>13</sup>C NMR CPMAS and dipolar dephasing experiments allowed us to complement the peak assignment by solution NMR and crystallographic information gathered by powder (degree of crystallinity) and single crystal X-ray diffraction (molecules per asymmetric unit). For instance, in the <sup>13</sup>C CPMAS trace of compound **1** four peaks were readily distinguished at ca. 110 ppm from the non-equivalent carbons C1, C1', C8 and C8', as expected since one molecule per asymmetric unit was obtained

 (Figure 5). In the case of compound **2**, slightly broader peaks were observed which was attributed to slightly lower crystallinity suggested by the PXRD analysis; yet, two alkyne signals C14 and C14' were detected at 90 ppm confirming the crystal symmetry (Z'=1).



Figure 5.<sup>13</sup>C NMR CPMAS experiments at room temperature of solvent free samples.

Lower resolution was observed in the <sup>13</sup>C spectrum of the phase **II** of compound **3**, showing overlapped peaks in all regions which was somehow expected given its elongated structure. Indeed, another reason for the broad peaks could be the combination of its moderate crystallinity suggested by PXRD and the low resolution of the magnetic field (75 MHz). Finally, in order to gain additional structural information a complementary <sup>15</sup>N CPMAS experiment of **3** at room temperature was acquired showing only one signal at 128 ppm, indicating that in this phase **II** the halves have little or none crystallographic differences.

# Activation energy to rotation by VT solid state <sup>2</sup>H NMR

Since variable temperature <sup>13</sup>C CPMAS experiments from 150 K to 435 K yielded only minor changes or they were possibly obscured due to overlapping signals (*Supporting Information*), we employed the deuterated analogs to explore solid state motion in the MHz regime using <sup>2</sup>H NMR. This technique has the advantage of probing the dynamics of the fragment under study as it is sensitive to the angular reorientations of the C-D bond.<sup>52</sup> Firstly, we studied all the

#### **Crystal Growth & Design**

isotopically enriched compounds where the deuterated phenyl rings are attached directly to the carbazole units. In these cases, the experiments from room temperature up to 415 K of compounds  $1-d_4$ ,  $2-d_8$  and the solvent free form of  $3-d_8$  showed a characteristic static Pake pattern,<sup>53</sup> leading us to conclude that they do not experience substantial rotation in crystals due to intra- and intermolecular steric effects (*Supporting Information*).



Figure 6. (a) Stacked experimental and simulated <sup>2</sup>H NMR spectra of compound **3-** $d_4$ . (b) 2-fold exchange model employed for simulations, (c) Arrhenius plot of  $\ln K_{rot}$  vs T<sup>-1</sup>.

After establishing that rotation of the aromatic rings linked to the carbazoles is not permitted, we studied the internal dynamics of the phenylene surrounded by two alkyne groups using the desolvated sample of isotopolog  $3-d_4$ . As mentioned before, voluminous groups are usually employed as stators in molecular rotors because they provide a cavity that allows rapid rotation of the inner fragment;<sup>29</sup> however, in the case of compound **3** the peripheral 9-phenylcarbazoles stators was not considered bulky enough to expect fast internal rotation. To our delight, at room temperature we observed a deuterium lineshape characteristic of a fast 180° exchange near the limit of detection of this technique (megahertz) which was confirmed by high temperature

#### **Crystal Growth & Design**

experiments that only slightly narrowed the lineshape. Subsequently, low temperature experiments were carried out to effectively reduce the frequency of this motion, as illustrated in Figure 6. These experimental lineshapes were successfully fitted using a two-fold model with a log-Gaussian distribution of rotational frequencies ( $\sigma$ =2)<sup>54</sup> in accordance with a sample of moderate crystallinity. From these simulations, a relatively low activation energy to rotation of *E<sub>a</sub>*=8.5 kcal/mol and an attempt factor of A= 1.1x10<sup>13</sup> s<sup>-1</sup> were obtained. These results indicate that crystallization does not completely restrict the internal motion in this flat rotor **3**, implying that compounds with similar architectures could have overlooked or underestimated dynamics.

# Solution and solid state fluorescence

Once the dynamic properties of the conjugated compounds 1-3 was explored, we set out to define their absorption and photoluminescence properties at room temperature. Spectra of compounds 1-3 were recorded both in solution and, in the solid state, using the same crystalline phases described above with the results listed in Table 1. In solution, all compounds presented intense absorption bands in the UV-region, particularly compounds 2 and 3 showed bands at 341 nm which can be attributed to the  $n \rightarrow \pi^*$  transition. Additionally, the photoluminescence spectra carried out in THF solution showed one intense band at 401 nm for compound 1, while a band at 402 nm was observed for compound 2 and at 417 nm for compound 3, with the red-shift attributed to the extended  $\pi$ -system (Figure 7).



Figure 7. Comparison of fluorescence spectra of compounds **1-3** in THF solution (dotted line) and in the solid state (solid line) using the crystalline forms described above.

In the case of solid state photoluminescence experiments, the crystalline samples of compounds **1** and **2** showed similar shapes as those observed in solution but with a significant reduction of their quantum yields from solution ( $\phi$ = 0.56 and 0.18, respectively) to powder ( $\phi$ = 0.09), attributed to the typical quenching due to aggregate formation.<sup>55-57</sup> On the other hand, the solid state emission spectrum of the phase **II** of rotor **3** is markedly different from that obtained in solution, showing two intense emission bands at 473 and 593 nm (Figure 7, blue solid line). Moreover, the quantum yield in the solid state ( $\phi$ = 0.28) was significantly improved when compared to that observed in THF solution ( $\phi$ = 0.06). The very low quantum yield of **3** in THF was attributed to the very fast motions occurring in solution, which include rotations and/or librations of several molecular fragments that may enable an efficient non-radiative channel causing the low quantum yield. Conversely, its crystallization reduced the frequency of the molecular motions occurring in solution resulting in the observed emission enhancement, allowing only the rotation of the central phenylene in the limit of the <sup>2</sup>H NMR technique, at MHz

#### **Crystal Growth & Design**

frequency. Additional variable temperature photophysical experiments in the solid state that would yield further information are currently unavailable for us but they will be pursued in future experiments.

Compound	λ <sub>max</sub> (nm) abs	λ <sub>em</sub> (nm) PL in solution	Stokes shift (cm <sup>-1</sup> )	ф Solution	ф powder
1	292	401	9.31E+03	0.56	0.09
2	341	402	4.45E+03	0.18	0.09
3	343	417	5.17E+03	0.06	0.28

# Gas phase computational studies of rotation

The MHz frequency of rotation observed in the phase **II** of compound **3** could be considered moderately fast in the field of molecular rotors, but is not fast enough to enable an efficient non-radiative pathway in these crystalline compounds, where solid state dynamics in the gigahertz  $(10^9)$  or terahertz  $(10^{12})$  will be required. In order to calculate what conditions would produce such interference between the two properties, we performed computational studies using the B3LYP basis set<sup>58,59</sup> to explore the energy requirements for the reorientations of the phenylene ring in the gas phase. The simulations were performed using the X-ray crystal coordinates and explored angular displacements on the phenylene rings with 15° steps. They indicated that while the central phenylene ring in compound **1** has a barrier to rotation as high as 29 Kcal/mol, the mobile component in compound **3** would require only 2 Kcal/mol, thanks to the low friction to rotation of the alkyne axis.

Considering the solid state <sup>2</sup>H NMR and theoretical results together, it seems very difficult that the steric effects over the phenylene ring in crystalline compound **1** would allow motion in a rate

that affects its emission in the solid. Conversely, compound **3** indeed may show faster rotation of the 1,4-diethynylphenylene fragment, but this is affected by intermolecular interactions that are not fully prevented by the relatively flat carbazole stator. Certainly, it is possible that a large increment of the temperature could increase the rotating frequency. If one assume that the rotational dynamics of **3** indefinitely follows the behavior described in the Arrhenius plot of Figure 6, it is possible to extrapolate the temperature at which the rotation would be in the gigahertz regime ( $10^9$  Hz), to approximately 450 K or higher. The studies presented here indicate that although the crystallinity and chemical structure of **3** would hold at that temperature; deuterium NMR would not detect further changes and other techniques to characterize solid state internal dynamics, i.e. relaxometry,<sup>60</sup> would be required.

#### Conclusions

In summary, the synthesis of a series of carbazole-[pi]-carbazole compounds **1-3** and their deuterated analogs was accomplished in good yields. Solid state techniques allowed us to characterize in detail the high crystallinity and slow or fast internal dynamics in these compounds. In particular, variable-temperature solid state <sup>2</sup>H NMR experiments led us to pinpoint which rings are unable to reorient within the crystals of all compounds, as well as to describe precisely the frequency of that which is highly mobile, *i.e.* the inner phenylene in the rotor **3**, which experiences rapid two-fold flips of 6 MHz at room temperature. In addition to solid state <sup>13</sup>C and <sup>2</sup>H NMR, photoluminescence experiments helped us define that this phase **II** encompasses for the first time a rapid rotary fragment and good solid state emission. Given the high thermal stability evidenced by DSC and TGA, this compound can be subjected to very high temperatures without loosing its crystallinity. Extensive photophysical studies for these

#### **Crystal Growth & Design**

compounds as well as synthetic modifications seeking faster solid state rotation in the GHz regime are currently underway.

# ASSOCIATED CONTENT

Supporting Information. Synthetic procedures, solution and solid state NMR spectra, X-ray diffraction refinement details, DSC, UVvis spectra in solution and computational details. CCDC deposit numbers 1462885, 1440776 and 1440777. This material is available free of charge via the Internet at http://pubs.acs.org.

# AUTHOR INFORMATION

#### **Corresponding Author**

\*brodriguez@iquimica.unam.mx.

# **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### **Funding Sources**

DGAPA PAPIIT-UNAM (IA200615) and CONACYT (238913)

#### ACKNOWLEDGMENTS

This work was financially supported by projects DGAPA PAPIIT-UNAM (IA200615) and CONACYT (238913). AAG thanks to CONACYT for the PhD scholarship 279212. We acknowledge the UCLA Department of Chemistry and Biochemistry for solid state <sup>2</sup>H NMR experiments. We thank the technical assistance from Dr. Francisco Javier Pérez Flores, Dr.

María del Carmen García Gonzalez, Q. María de los Ángeles Peña González and M. C. Elizabeth Huerta Salazar (MS and NMR).

#### REFERENCES

1. Han, K.-L., Zhang, X.; Yang, M.-J. Protein Conformational Dynamics; Springer: Switzerland, 2014.

2. Watson, M. A.; Cockroft, S. L. Chem. Soc. Rev. 2016, DOI: 10.1039/c5cs00874c.

3. Erbas-Cakmak, S.; Leigh, D. A.; McTernan, C. T.; Nussbaumer, A. L. Chem. Rev. 2015, 115, 10081.

4. Abendroth, J. M.; Bushuyev, D. S.; Weiss, P. S.; Barrett, C. J. ACS Nano 2015, 9, 7746.

5. Pawle, R. H.; Hass, T. E.; Müller, P.; Thomas S. W. Chem. Sci. 2014, 5, 4184.

6. Bleger, D. Macromol. Chem. Phys. 2016, 217, 189.

7. Sagara, Y.; Yamane, S.; Matani, M.; Weder, C.; Kato, T Adv. Mater. 2016, 28, 1073.

8. Zhang, Y.; Barboiu, M. Chem. Rev. 2016, 116, 809.

9. Tanaka, T.; Osuka, A. Chem. Soc. Rev. 2015, 44, 943.

10. Mutai, T.; Satou, H.; Araki, K. Nat. Mater. 2005, 4, 685.

11. Kottas, G. S.; Clarke, L. L.; Horinek, D.; Michl, J. Chem Rev. 2005, 105, 1281.

12. Mei, J.; Leung, N. L. C.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. Chem. Rev. 2015, 115, 11718.

13. Yan. D.; Yang, H.; Meng, Q.; Lin, H.; Wei, M. Adv. Funct. Mater. 2014, 24, 587.

14. Mei, J.; Ho 5429.	ng, Y.; Lam, J. W. Y.; (	Qin, A.; Tang, Y.; T	<sup>C</sup> ang, B. Z. <i>Adv. Mo</i>	ater. <b>2014</b> , 26,
15. Fan, G.; Yai	ng, X.; Liang, R.; Zhao, J	.; Li, S.; Yan, D. <i>Cr</i> y	ystEngComm, <b>2016</b> ,	18, 240.
16. Tong, J.; W 21875.	Vang, Y. L.; Wang, Z.; S	Sun, J Z.; Tang, B.	Z. J. Phys. Chem.	C <b>2015</b> , <i>119</i> ,
17. Han, T.; Fer	ng, X.; Chen, D; Dong, Y	J. Mater. Chem. C.	<b>2015</b> , <i>3</i> , 744.	
18. Yan, D.; Eva	ans, G. D. <i>Mater. Horiz.</i> 2	<b>2014</b> , <i>1</i> , 46.		
19. Li, J.; Zhai 907.	ng, Y.; Mei, J.; Lam, J. V	W. Y.; Hao, J.; Tan	g, B. Z. Chem. Eur	: J., <b>2015</b> , 21,
20. Parrott, E. I <i>Mater. Horiz.</i> , <b>20</b>	P. J.; Tan, N. Y.; Hu, R.; <b>14</b> , <i>1</i> , 251.	Zeitler, J. A.; Tang	g, B. Z.; Pickwell-M	facPherson, E.
21. Shustova, N J. Am. Chem. Soc.	I. B.; Ong, TC.; Cozzoli ., <b>2012</b> , <i>134</i> , 15061.	no, A. F.; Michaelis	s, V. K.; Griffin, R.	G.; Dinca, M.
22. Kaleta, J:, I Chem. <b>2015</b> , 80, 6	Dron, P. I.; Zhao, K.; Sh 5173.	en, Y.; Císarová, I.;	; Rogers, C. T.; Mi	ichl, J. J. Org.
23. Kaleta, J.; M A.; Canadell, E.; I	Michl, J.; Mézière, C.; Sin Batail, P. <i>CrystEngComm</i>	nonov, S.; Zorina, I , <b>2015</b> , <i>17</i> , 7829.	L.; Wzietek, P.; Roo	lríguez-Fortea,
24. Kobr, L.; Sl 14, 559.	hen, Y.; Shoemaker, R. H	K.; Rogers, C. T.; M	lichl, J. <i>Cryst. Gro</i> v	wth Des. 2014,

25. Comotti, A.; Bracco, S. Yamamoto, Y.; Beretta, M.; Hirukawa, T.; Tohnai, N.; Miyata, M.; Sozzani, P. J. Am. Chem. Soc. 2014, 136, 618.

26. Comotti, A.; Bracco, S.; Valsesia, P.; Beretta, M.; Sozzani, P. Angew. Chem. Int. Ed. 2010, 49, 1760.

27. Pérez-Estrada, S.; Rodríguez-Molina, B.; Xiao, L.; Santillan, R.; Jimenez-Oses, G.; Houk,
K. N.; Garcia-Garibay, M. A. J. Am. Chem. Soc., 2015, 137, 2175.

28. Commins, P.; Garcia-Garibay, M. A. J. Org. Chem. 2014, 79, 1611.

29. Vogelsberg C. S.; Garcia-Garibay, M. A. Chem. Soc. Rev. 2012, 41, 1892.

30. Lemouchi, C.; Yamamoto, H. M.; Kato, P.; Simonov, S.; Zorina, L.; Rodríguez-Fortea, A.; Canadell, E.; Wzietek, P.; Iliopoilos, K.; Gindre, D.; Chrysos, M.; Batail, P. *Cryst. Growth, Des.* **2014**, *14*, 3375.

31. Lemouchi, C.; Iliopoulos, K.; Zorina, L.; Simonov, S.; Wzietek, P.; Cauchy, T.; Rodríguez-Fortea, Enric Canadell, E.; Kaleta, J.; Michl, J.; Gindre, D.; Chrysos, M.; Batail, P. *J. Am. Chem. Soc.* **2013**, *135*, 9366.

32. Nishiyama, Y.; Inagaki, Y.; Yamaguchi, K.; Setaka W. J. Org. Chem. 2015, 80, 9959.

33. Setaka, W.; Inoue, K.; Higa, S.; Yoshigai, S.; Kono, H.; Yamaguchi, K. J. Org. Chem.2014, 79, 8288.

34. Prack, E.; O'Keefe, C. A.; Moore, J. K.; Lai, A.; Lough, A. J.; Macdonald, P. M.; Conradi,
M. S.; Schurko, R. W.; Fekl, U. J. Am. Chem. Soc. 2015, 137, 13564.

#### **Crystal Growth & Design**

35. Sakai, K.-I.; Tsuchiya, S.; Kikuchi, T.; Akutagawa, T. J. Mater. Chem. C 2016, DOI:10.1039/c5tc04290a.

36. Zhang, Q.-C.; Takeda, T.; Hoshino, N.; Noro, S.-i.; Nakamura, T.; Akutagawa, T. *Cryst. Growth Des.* **2015**, *15*, 5705.

37. Akutagawa, T.; Nakamura, T. Dalton Trans. 2008, 6335.

38. Hughs, M.; Jimenez, M.; Khan, S. I.; Garcia-Garibay, M. A. J. Org. Chem. 2013, 78, 5293.

39. Xue, P.; Sun, J.; Chen, P.; Gong, P.; Yao, B.; Zhang, Z.; Qian, C.; Lu, R. *J. Mater. Chem. C* **2015**, *3*, 4086.

40.Ding, J.; Zhang, B.; Lu, J.; Xie, Z.; Wang, L.; Jing, X.; Fosong Wang, F. Adv. Mater. 2009, 21, 4983.

41. Yu, M.; Wang, S. Shao, S.; Junqiao Ding, J. Wang, L. Jinga, X.; Wang. F. *J. Mater. Chem. C* **2015**, *3*, 861.

42. Sun, K.; Jiang, W.; Ban, X.; Huang B.; Zhang Z.; Ye, M.; Sun, Y. Adv. 2016, 6, 22137.

43. Shilh, C.-H.; Rajamalli, P.; wu, C.-A.; Hsieh, W.-T.; Cheng, C.-H. *Appl. Mater. Interfaces* **2015**, *7*, 10466.

44. Kim, D.; Coropceanu, V.; Brédas, J.-L. J. Am. Chem. Soc. 2011, 133, 17895.

45. *Fundamentals of Solid-State Lighting*. Khanna, V. K. Boca Raton, FL, USA, CRC Press, 2014.

46. Albrecht, K.; Matsuoka, K.; Fujita, K.; Yamamoto, K Angew. Chem. Int. Ed. 2015, 54, 5677.

47. Adhikari, R.; Neckers, D. C.; Shah, B. K. J. Org. Chem. 2009, 74, 3341.

48. Zhang, Q.; Chen, J.; Chen, Y.; Wang, L.; Ma D.; Jing, X.; Wang, F. J. Mater. Chem. 2004, 14, 895.

49. Kaafarani, B. R.; El-Ballouli, A. O.; Trattnig, R.; Fonari, A.; Sax, S.; Wex, B.; Risko, C.; Khnayzer, R. S.; Barlow, S.; Patra, D.; Timofeeva, T. V.; List, E. J. W.; Brédas J.-L.; Marder, S. R. *J. Mater. Chem. C* **2013**, *1*, 1638.

50. Ohkita, M.; Endo, A.; Sumiya, K.; Nakanotani, H.; Suzuki, T.; Adachi, C. *J. Lumin.* **2011**, *131*, 1520.

51. Jenkis, R.; Snyder, R. L. Introduction to X-ray powder diffractometry; Wiley: New York, 1996.

52. Wasylishen, R. E.; Ashbrook, S. K.; Wimperis, S. NMR of Quadrupolar Nuclei in Solid Materials; Wiley: West Sussex, United Kingdom, 2012.

53. Duer, M. J. Introduction to solid-state NMR spectroscopy; Blackwell: Oxford, United Kingdom, 2004.

54. Macho, V; Brombacher, L; Spiess, H. W. Appl. Magn. Reson. 2001, 20, 405.

55. Ma, X.; Sun, R.; Cheng, J.; Liu, J.; Gou, F.; Xianf, H.; Zhou, X. J. Chem. Educ. 2016, 93, 345.

2
3
4
4
5
6
7
0
0
9
10
11
12
12
13
14
15
16
17
17
18
19
20
21
∠ I 00
22
23
24
25
20
26
27
28
20
29
30
31
32
33
33
34
35
36
37
57
38
39
40
<u>4</u> 1
40
42
43
44
45
16
40
47
48
49
50
50
51
52
53
54
54
55
56
57
58
50
59
60

56. Chen, G.; Li, W.; Zhou, T.; Peng, Q.; Zhai, D.; Li, H.; Yuan, W. Z.; Zhang, Y.; Tang, T. *Adv. Mater.* **2015**, *27*, 4496.

57. Aldrep, M. P.; Li, C.; Zhang, G.-F.; Gong, W.-L.; Li, A. D. Q.; Dai, Y.; Ma, D.; Zhu, M.-Q. J. Mater. Chem. 2012, 22, 75.15.

58. Becke, A. D. J. Chem. Phys. 1993, 98, 5648.

59. Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B Condens. Matter Mater. Phys. 1988, 37, 785.

60. Bakhmutov, V. I. Practical NMR Relaxation for chemists; Wiley, Chichester, United Kingdom, 2004.

# FOR TABLE OF CONTENTS USE ONLY

# Synthesis of a carbazole-[pi]-carbazole molecular rotor with fast solid state intramolecular dynamics and crystallization-induced emission.

Andrés Aguilar-Granda, Salvador Pérez-Estrada, Arian E. Roa, Joelis Rodríguez-Hernández, Simón Hernández-Ortega, Mario Rodriguez, and Braulio Rodríguez-Molina.



Variable temperature solid-state <sup>2</sup>H NMR, X-ray studies and photoluminescence experiments allowed us to characterize in detail the synthetic rotor **3** that shows fast internal dynamics in the MHz regime and enhanced fluorescence of its crystals ( $\phi = 0.28$ ), after a phase transition from a benzene solvate (phase I) to a highly stable solvent free crystalline form (phase II).