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## Crystalline arrays of molecular rotors with TIPS-trityl and phenolic-trityl stators using phenylene, 1,2-difluorophenylene and pyridine rotators

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In this work, we describe the synthesis and solid-state characterization of a series of molecular rotors with *tri*-isopropylsilyloxy-substituted (TIPS) trityl stators axially linked to 1,4-diethynylphenylene, 3,6-diethynyl-1,2-difluorophenylene and 2,5-diethynylpyridine rotators to produce 1,4-bis[(3,3-diphenyl-3-(3'-*tri*-isopropylsilyloxy)-phenyl)-prop-1-yn-1-yl]benzene (**1**), 1,4-bis[(3,3-diphenyl-3-(3'-*tri*-isopropylsilyloxy)-phenyl)-prop-1-yn-1-yl]-2,3-difluorobenzene (**2**) and 2,5-bis[(3,3-diphenyl-3-(3'-*tri*-isopropylsilyloxy)-phenyl)-prop-1-yn-1-yl]pyridine (**3**). The subsequent removal of the TIPS protecting group led to their corresponding hydroxyl-substituted trityl derivatives (**4**) and (**5**). TIPS- and HO-substituted stators are involved in different inter- and intramolecular interactions (hydrogen bonds, phenyl embraces, C-H- $\pi$  interactions) that give rise to isomorphic packing motifs that constrained the rotational dynamics in the solid-state to the slow exchange regime.

### Introduction

The fascinating and complex operation of biomolecular machines has inspired a large amount of research dedicated to the development of synthetic molecular assemblies that can show a response to an external stimuli.<sup>1</sup> It has been proposed that the function of artificial molecular machines could possibly emulate those found in Nature, such as the skeletal muscle or the ATPase, when based on the collective action of their molecular components.<sup>2-3</sup> Keeping in mind that the function of those biomolecular machines occurs in condensed media, during the past years our research has been focused on the development of *amphidynamic crystals*: solid materials by design in which specific molecular components experience motion within rigid bulky components that form an ordered crystal lattice.<sup>4a</sup> We amongst others, have suggested that the

precise knowledge about the internal dynamics may offer a new perspective in the field of functional solid materials, for example in Metal Organic Frameworks (MOFs) or Periodic Mesoporous Organosilicas (PMOs). Additionally, those engineered solids may represent a promising entry as molecular switches in condensed media, with potential optoelectronic<sup>5</sup> or photonic<sup>6</sup> applications.

In order to obtain amphidynamic crystals, the current design relies on the synthesis and characterization of molecular rotors, dumbbell-like molecules built up with three elements: *rotator* (the mobile component), *axle* and *stator* which is often the bulky group that acts as the shielding framework for the system.<sup>7</sup> Several variations of these components have been explored in the past in order to provide an enhanced dynamic behavior.<sup>8</sup> Furthermore, the available theoretical and experimental evidence has shown the enormous influence of crystal packing in the dynamic behavior,<sup>9</sup> an interesting example being the BIBCO rotor (1,4-bis-(iodoethynyl)bicyclo[2.2.2]octane), in which the same molecule experiences two distinct rotational dynamics in the solid state.<sup>10</sup>

Efforts devoted to control the frequency of the internal motion comprise the study of several stator structures, which include substituted triptycenes,<sup>8</sup> substituted trityl groups,<sup>14</sup> steroids,<sup>4c,d</sup> and porous solids such as MOFs.<sup>11</sup> These molecules tend to pack less densely (often with solvent molecules),<sup>12</sup> in a way that facilitates the dynamic behavior in the solid state.<sup>13</sup>

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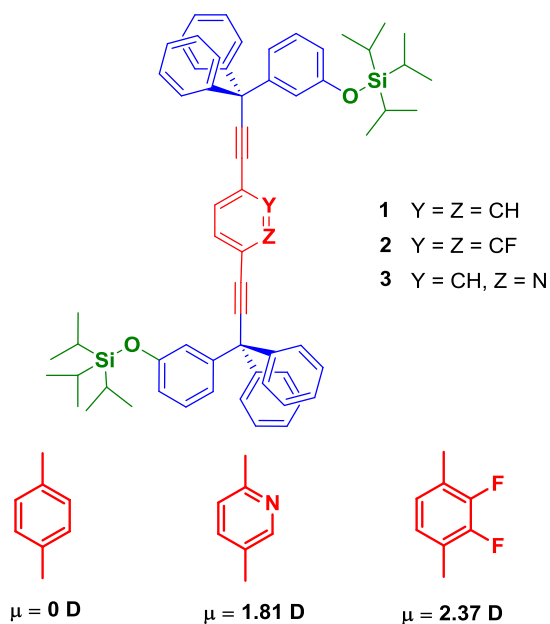
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Electronic Supplementary Information (ESI) available: Synthetic procedures, <sup>1</sup>H and <sup>13</sup>C spectral data, ss NMR data, PXRD data, DSC and TGA. Crystallographic data for the structures in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 943819 (**4a**-acetone), 943820 (**4b**-methanol), 943821 (**4c**-DMSO), 943496 (**2**) and 943497 (**1**), these data can be obtained free of charge from the The Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data\_request/cif. See DOI: 10.1039/b000000x/

With that in mind, in a previous report we synthesized a family of compounds with voluminous *tert*-butyldiphenylsilyl-protected (TBDPS) triphenylmethyl stators to evaluate their effect on the rotator dynamics.<sup>14</sup> From these studies, we reported the use of large TBDPS groups to promote rotational dynamics; however, the intramolecular interactions between the phenyl rings of these bulky groups and the rotator shut down the awaited internal motion. Additionally, in such a previous set of molecular rotors the severe disorder of the *tert*-butylsilyl groups and the low stability and quality of the crystals prevented a detailed analysis of the molecular structure.



**Figure 1.** Molecular rotors reported here based on *tri*-isopropylsilyloxy-substituted trityl stators.

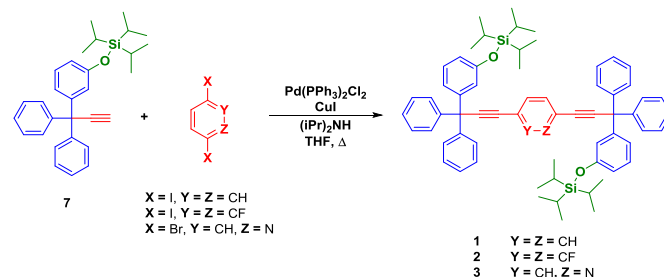
While fast rotations could indeed be interesting, slow molecular dynamics can also induce large effects as those resulting from the large conformational changes of proteins.<sup>15</sup> Those premises guided us to develop a new series of compounds using similar protecting groups. Consequently, here we report the synthesis, characterization and crystallization of molecular rotors **1**, **2** and **3** (Figure 1). In comparison with the TBPDS-protected stators, the TIPS groups produced stable crystalline samples that allowed the detailed study of the molecular structure and packing environment. We also employed different rotators in order to gain further insights about the stability, crystal growth and intermolecular interactions in these molecules.

## Results and Discussion

### Synthesis and solution characterization.

We employed *tri*-isopropylsilyloxy-substituted trityl groups as stators due to their moderate size and good stability under different conditions. These TIPS-groups were placed in *meta*-

position following the convergent protocol (Figure 1).<sup>14</sup> The stators with one TIPS unit per molecule provided samples with good stability, and the subsequent increase in the number of TIPS units disfavoured crystallinity, forming oily (2 TIPS per stator) and liquid samples (3 TIPS per stator) (see ESI). Those compounds were fully characterized but difficult to crystallize and will not be described in detail here.



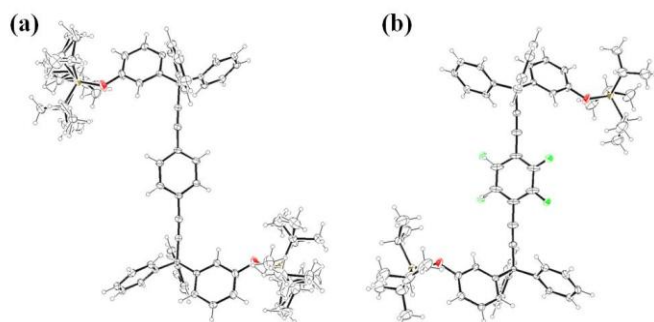
**Scheme 1.** Synthesis of molecular rotors **1-3**.

Next, we have focused in the introduction of polar substituents in the central part with the aim to explore isomorphic crystallization to create compounds capable of providing physical and chemical properties that change as a result of reorienting dipoles under the influence of external fields. The selected pyridine and difluorobenzene rotators contain calculated dipoles of *ca.* 1.81 and 2.37 D, respectively.<sup>16</sup> Molecular rotors with TIPS-substituted trityl stators **1-3** were synthesized using Sonogashira cross coupling conditions with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and CuI as catalysts. The TIPS-substituted trityl **7** (see ESI) was reacted with 1,4-diiodobenzene, 2,3-difluoro-1,4-diiodobenzene and 2,5-dibromopyridine to produce molecular rotors **1** (77 %), **2** (82 %), and **3** (81 %) in good yields as shown in scheme 1. The synthesis of molecular rotors **1-3** was corroborated by solution NMR experiments, where the <sup>1</sup>H-NMR spectrum of **1** showed a singlet at  $\delta = 7.49$  ppm, corresponding to the hydrogen atoms of the phenylene rotator. For the fluorinated derivative **2**, the spectrum showed a multiplet between  $\delta = 7.21$ -7.19 ppm for the two hydrogens of the aromatic rotator, due to the hetero-(H-F) and homonuclear (H-H) coupling. In the proton spectrum of **3**, the three signals at  $\delta = 8.66$ , 7.76 and 7.35 ppm evidenced the incorporation of the pyridine rotator. Additionally, the <sup>29</sup>Si-NMR verified the presence of the TIPS groups, with single signals between  $\delta = 16.0$ -16.2 ppm for all the compounds. The observed peaks at *m/z* 9555.5301 (**1**), 991.5111 (**2**) and 959.5661 (**3**) from high resolution mass spectrometry analyses were in accordance with the expected molecular ions.

### Solid-state characterization.

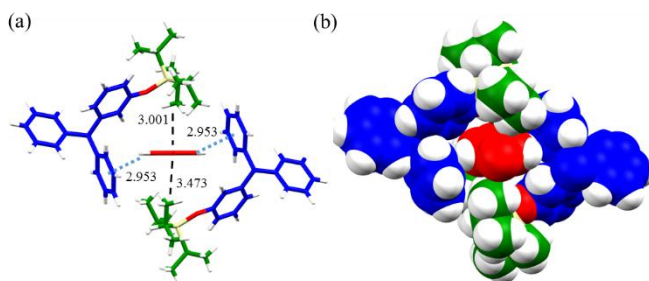
*Single X-Ray crystal studies of 1 and 2.* Single crystals suitable for XRD of molecular rotor **1** and its fluorinated analogue **2** were grown as solvent-free needles by slow evaporation from chloroform solutions in partially open glass vials (Figure 2). As anticipated, the crystal structures of both compounds grew isomorphic and crystallize in the orthorhombic Pccn space group. Their crystallographic cell constants and angles differ

only slightly with the relevant parameters compiled in Table 1 (see ESI).



**Figure 2.** Molecular structures of compound a) **1** and b) **2**, thermal ellipsoids are drawn at 30% probability level for all atoms other than H.

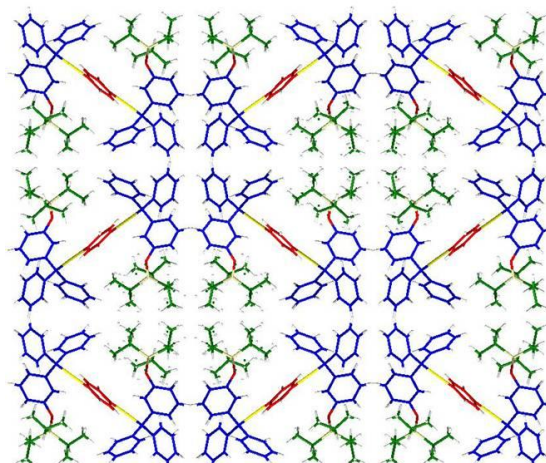
The asymmetric unit of both **1** and **2** contains only half of the molecule and the other half is generated by an inversion center that lies on the center of the 1,4-diethynylphenylene rotator. This is somehow expected considering that molecules having inversion symmetry occupy Wickoff positions of  $C_i$  symmetry 99 % of the times according to a study based on CSD.<sup>17</sup> In the case of compound **1**, the TIPS-group in the stator was disordered over two sites (occupancy 50:50). On the other hand, compound **2** did not show disorder in the TIPS-group, but instead we observed a disorder of the fluorinated rotator over two positions, which was modeled with a 50:50 occupancy. This prompted us to further investigate the nature of the disorder, given that solid state NMR can distinguish between static and dynamic disorder among partially occupied sites. This aspect will be discussed in a subsequent section.



**Figure 4.** a) Cross section view of **1** highlighting close contacts around the central phenylene unit b) space filling model of the environment around the rotator.

As an initial assessment of the factors that might affect the solid state dynamics, we performed a search of close contacts around the rotator in **1** as illustrated in the cross section view in Figure 4. This analysis revealed a crowded environment around the rotator with two isopropyl fragments (in green) above and below of the rotator (in red), with methyl-phenyl distances of 3.001 and 3.473 Å, respectively. Additionally, up to two *edge to face* interactions of this phenylene with neighboring stators (in blue) could be observed, both showing CH-centroid distances of 2.953 Å. Similar distances were found in compound **2**. These distances are indicative of a small

crystal cavity which may suggest high activation barriers to rotation that would be discussed in the following sections.



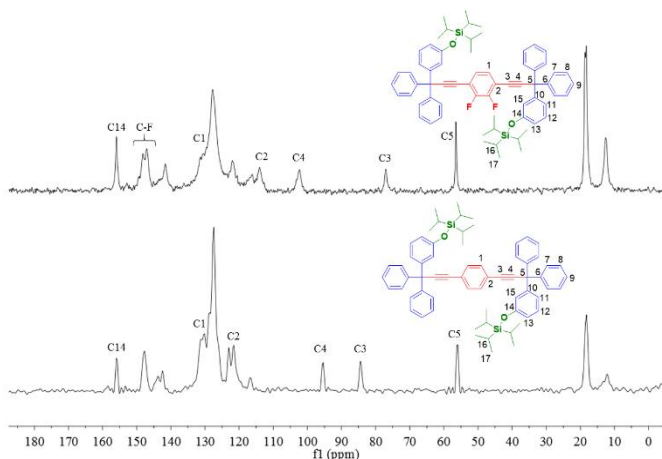
**Figure 3.** Crystal packing of the isomorphous packing in compounds **1** and **2**, viewed down the crystallographic  $c$  axis.

The crystal packing of compounds **1-2** can be described as columnar arrangement of parallel displaced array of molecular rotors along the crystallographic  $c$  axis (more accurately, described considering the rotation and translation involved by the presence of a  $c$  glide plane). These columnar arrangements are held together by various *edge to face* interactions that could be classified as parallel fourth-fold phenyl embraces<sup>15</sup> between three neighboring molecules in which two aromatic rings of one stator interact with two different rings of the other two stators (figure 3).

**Calorimetric and PXRD studies of molecular rotors.** Crystalline samples of compounds **1** and **2** were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to ascertain their thermal stability upon heating in the range 30-300 °C (see ESI). In the DSC experiments, only one endothermic peak was observed at 166.4 °C for compound **1** and at 132.8 °C for **2**, which were attributed to their respective melting points, in agreement with the visual determination. Accordingly, only minor changes in the traces of both compounds (corresponding to a weight loss of *ca.* 1 %) were observed in the TGA experiments in a temperature range that coincides with the melting point. These analyses indicate that the samples do not contain any significant amount of solvent trapped within their lattices and that they decompose above the melting point. Additionally, powder XRD analyses were employed to corroborate the crystallinity of the bulk samples of **1** and **2**. The experimental PXRD patterns with sharp peaks in 5-50 ( $2\theta$  degrees) range matched very well with the calculated ones from the single crystal X-ray data.

**Solid state NMR studies of molecular rotors 1 and 2.** It is well known that the dynamics among fully populated sites is difficult to identify in single crystal X-ray diffraction experiments. The little or absence of temporal information is a result of the long range spatial and time average nature of

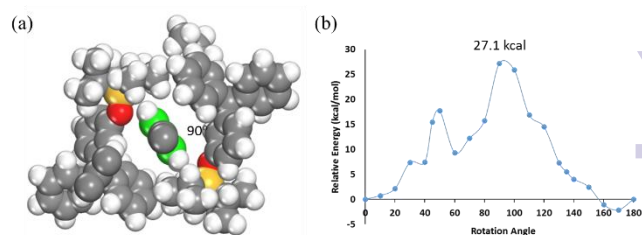
information given by standard X-ray studies.<sup>18</sup> In order to explore possible internal dynamics and further characterize the synthesized molecular rotors, we performed <sup>13</sup>C-NMR by using the Cross Polarization Magic Angle Spinning technique. This tool is useful to identify between different solid forms of the same compound and to distinguish the chemical shift differences between different compounds with isomorphic crystals, as reported here.



**Figure 5.** <sup>13</sup>C NMR spectra of compounds **1** (bottom) and **2** (top) under CPMAS conditions.

In agreement with the X-ray diffraction data that indicates only one half of the molecule per asymmetric unit, the solid-state <sup>13</sup>C-NMR spectra of **1** and **2** showed signals that accounted only for half of their respective molecules, demonstrating that the two halves of the molecular rotors are crystallographically equivalent, sharp peaks confirmed the crystallinity of the samples (figure 5). Noticeable differences in the chemical shifts can be observed in signals closer to the central aromatic ring when comparing crystalline molecular rotors **1** and **2** due to the effect of the halogen atoms. The signals were assigned by chemical shifts analysis and by comparison with the solution NMR data. Given the low resolution obtained at 7.05 T, we obtained overlapped signals of the central carbons of **1** and **2** with the trityl carbons between 135-125 ppm, which made it impractical to extract dynamic information and prevented further VT experiments.

As a qualitative complement, we carried out <sup>13</sup>C CPMAS Dipolar Dephasing experiments that are designed to remove all protonated signals except those involved in a dynamic process with an exchange frequency higher than the C-H heteronuclear coupling (ca. 20 KHz). Given the fact that all the CH signals were absent in this spectrum, we concluded that only a slow exchange process is taking place. We were able to confirm those results and obtain an upper limit to rotation by acquiring a solid state <sup>2</sup>H NMR spectrum using a deuterated analog **1-d<sub>4</sub>**. Based on the <sup>2</sup>H line shape at room temperature, we observed that any motion present in compounds **1** or **2** would take place at frequencies not higher than 10 KHz (see ESI for synthetic and spectroscopic details).

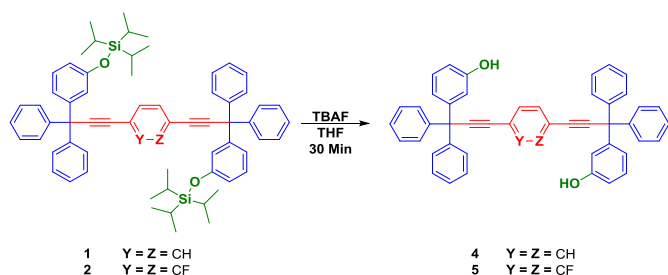


**Figure 6.** a) Snapshot of the MM computational analysis carried out where the central phenyl ring in **1** approaches the TIPs groups, b) Plot of the calculated potential showing the energy every 10° steps.

Our spectroscopic results were supported by a computational analysis where the rotational coordinate of the rotator was explored using molecular mechanics methods, since these are known to provide reasonable conformational analysis while being computationally accessible for large systems. The COMPASS force field with Fine convergence criteria was used for all the geometry optimizations. Notably, the computed energy minimum structure is very close to the experimental X-ray structure. Angular displacements of 10° led to the energy profile shown in Figure 6. Given the crystallographic symmetry of the phenylene group, the analyses were restricted to half a rotational cycle, i.e. 180°. To better represent the local environment of a rotor in the crystal, a cluster of three neighbouring molecules was extracted from the X-ray data.

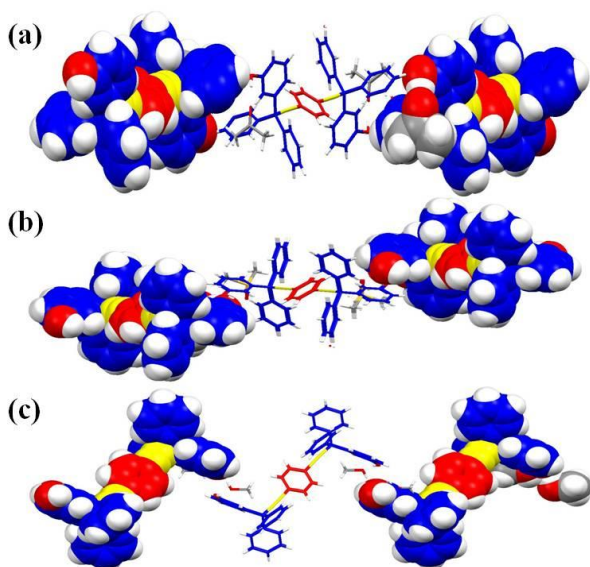
In this conformation, an edge-to-face cooperative stacking is observed. Since electron correlation effects (and thus, dispersive forces) are not explicitly computed in molecular mechanics, the stabilizing interaction is expected to be mainly electrostatic in nature. In the case of compound **1** when the angular displacement approaches 50° a local maximum of ca. 18 kcal/mol is reached. Close exploration of this conformer indicates some steric interactions with the isopropyl groups. Nevertheless, a maximum in potential energy of 27 kcal/mol was calculated when the phenylene group explores 90° rotation. Even though this very high calculated energy could be lowered taking into account additional conformational changes of the surrounding molecules, we anticipate that the resulting energy would be still high compared with similar molecular rotors showing barriers to rotation in the range of 12-14 kcal/mol,<sup>15</sup> evidencing that angular displacements in **1** or **2** result in an energetically costly conformation resulting from the destabilization of the edge-to-face and the interactions with the bulky TIPS groups.

**Phenolic derivatives 4 and 5.** As the final part of our study with silyl-protected molecular rotors, compounds **1-2** were subsequently deprotected to afford highly crystalline phenolic derivatives **4** (88 %), and **5** (88 %), that were fully characterized in solution and were synthesized in order to study the behavior of stronger supramolecular interactions in the crystal packing such as hydrogen bonds, (Figure 7).



**Scheme 2.** Synthesis of molecular rotors **4** and **5**.

After removal of protecting groups, three solvates of **4** in acetone (**4a**), methanol (**4b**) and DMSO (**4c**) were characterized by means of single crystal X-ray diffraction experiments, all of them in the P-1 space group trapping two solvent molecules per molecule of **4**. Crystallization of solvates from compound **5** were obtained but they had poor quality for X-ray single crystal studies and they are not described here. A comparison between the molecular geometries of compound **4** in solvates **4a**, **4b**, and **4c**, revealed only slight changes, in all of them the groups are placed in an *anti*-fashion with respect to the alkyne axis (figure 7). The three molecules show slight deviations from the geometry of an ideal diethynylphenylene fragment<sup>19</sup> with the differences in their conformations (see ESI) arising from interactions present in each solid form, and most important, reflect the complementary effect between classic hydrogen bonding and phenyl embraces, resulting in a conformational adjustment in the crystal packing.<sup>20,21</sup>



**Figure 7.** Crystal packing of solvates **4** in (a) acetone **4a**, (b) DMSO **4c** and (c) methanol **4b**, view along *b* axis.

The similarities between acetone and DMSO solvates allow to treat these two solids as one, in both forms there is a balance between hydrogen bonding (O1-H...O2) and parallel fourth-phenyl embrace (P4PE) in which the ring that participates in the C-H... $\pi$  interaction is distorted from the ideal T geometry presumably to favor the hydrogen bond. The absence of this

P4PE in the methanol clathrate could be attributed to the stabilization that provides the sigma cooperativity (figure 8) that accompanies the homodromic cycle of four hydrogen bonds, corresponding to a graph set notation  $R_4^4(8)$ .

## Conclusions

In conclusion, three new molecular rotors **1**, **2** and **3** based on TIPS-substituted trityl stators and two deprotected rotors **4** and **5** were synthesized and characterized in solution and in the solid state. Isomorphic crystal arrays of compounds **1** and **2** were obtained upon slow evaporation, whereas compound **3** decomposes over time. Moreover, the analyses of three different solvates **4a-c** of molecular rotor **4** showed the complementarity between classic hydrogen bonds and phenyl embraces.

Regarding the molecular dynamics of **1** and **2**, we were able to correlate the results from <sup>13</sup>C and <sup>2</sup>H solid state NMR with X-ray and computational models to conclude that very high barriers to rotation are the result of the steric effect with the TIPS groups and the stabilizing *edge to face* interactions with the surrounding phenyl groups, only allowing rotational dynamics with frequencies lower than 10 KHz.

## Experimental

**General.** All the reactions were carried out under an inert atmosphere (Nitrogen or Argon). The starting materials were purchased from commercial suppliers and used as received. Tetrahydrofuran (THF) was distilled from sodium-benzophenone in a continuous still under an atmosphere of nitrogen. Analytical thin-layer chromatography (TLC) was performed using pre-coated TLC-sheets ALUGRAM Xtra S<sub>18</sub> G/UV<sub>254</sub> silica gel 60 with fluorescent indicator. Flash column chromatography was performed using silica gel (230-400 mesh) as the stationary phase. Melting points were determined on a melting point apparatus using open glass capillaries and are uncorrected. The IR spectra were recorded with the Attenuated Total Reflectance as solid samples, or using KBr pellets and the units are stated as cm<sup>-1</sup>. Mass spectrometry data were collected using Fast Atom Bombardment (+) technique. High resolution mass spectrometry data were obtained using Atmospheric Pressure Chemical Ionization (APCI) with a Time-of-Flight (TOF) detector. Thermal analyses were realized on a Calorimeter DSC821<sup>e</sup> and Thermobalance TGA/SDTA851<sup>e</sup>. Solution <sup>1</sup>H-NMR spectra were recorded at 270, 300, 400 and 500 MHz and solution <sup>13</sup>C-NMR spectra were recorded at 67.9, 75.5, 100 and 125 MHz. All the chemical shifts ( $\delta$ ) are reported in ppm with respect to TMS using residual solvent as reference. The coupling constants (*J*) are reported in Hz. Multiplicities signals are reported as: singlet (s), doublet (d), doublet-doublet (dd), doublet-triplet (dt), sextuplet (sext), multiplet (m). NMR solid state experiments were obtained on a Bruker 300 Avance II spectrometer operating at a frequency of 46.07 MHz, using a Bruker 4 mm wide-line probe. Single crystal X-ray diffraction analyses of **1**, **2** and **4a** were performed on a Enraf Noni s

Kappa-CCD ( $\lambda$  MoK $\alpha$  = 0.71073 Å, graphite monochromator, T = 298 K-CCD), at 173(K). The collection of **4b** and **4c** was done at 173 (K), on a Bruker SMART APEX II CCD Platform (UCLA). All reflection data set were corrected for Lorentz and polarization effects. The crystals were mounted on conventional MicroLoops™. The first structure solution was obtained using the SHELXS-97<sup>22</sup> or SIR2004<sup>23</sup> programs and then the SHELXL-97 program was applied for refinement and output data. All software manipulations were done under the WinGX<sup>24</sup> environment program set. All heavy atoms were found by Fourier map difference and refined anisotropically. X-ray powder diffraction analyses were realized on a Siemens D5000 K $\alpha$  Cu  $\alpha$  = 1.5404Å, 35kV, 30mA. X-ray powder diffraction analyses were realized on a Siemens D5000 K $\alpha$  Cu  $\alpha$  = 1.5404Å, 35kV, 30mA.

**Synthetic procedure for [(3-*tri*-isopropylsilyloxy)phenyl]3,3,-diphenyl-propyne (**7**).** Hydrochloric acid was slowly bubbled to a solution of diphenyl[3-(*tri*-isopropylsilyloxy)phenyl]methanol **II** (1.00 g, 2.3 mmol), in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) at room temperature. After 5 h stirring, the solvent was removed at reduce pressure and the solid obtained was redissolved in benzene (25 ml), then, ethynylmagnesium bromide (5.1 ml, 0.7 M in THF, 3.6 mmol) was added and the mixture was stirred for 48 h. After this time, the reaction was quenched by addition of saturated NH<sub>4</sub>Cl, and the organic phase was extracted twice with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic portions were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Purification on silica gel with hexane yielded compound **7** as yellow oil (0.60 g, 59 %). IR (KBr) ( $\nu$ , cm<sup>-1</sup>): 3061, 2945, 2867, 2345, 1597, 1484, 1429, 1386, 1276, 1145, 976, 882, 766, 700, 640, 569, 509, 459. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.38-7.26 (10H, m), 7.23 (1H, t,  $J$  = 7.9 Hz), 7.03 (1H, d,  $J$  = 7.9 Hz), 6.87 (1H, dd,  $J$  = 7.5, 2.2 Hz), 2.73 (1H, s), 1.24-1.13 (3H, m), 1.08 (18H, d,  $J$  = 6.6 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 155.9, 146.2, 145.0, 129.2, 129.1, 128.1, 127.0, 122.0, 121.2, 118.8, 89.9, 73.3, 55.5, 18.0, 12.7. <sup>29</sup>Si-NMR (79.42 MHz, CDCl<sub>3</sub>)  $\delta$ : 16.1 ppm. HRMS (APCI-TOF), Calcd for C<sub>30</sub>H<sub>37</sub>OSi 441.2608. Found 441.2612. Error 0.99 ppm. MS (DIP): 440 (M<sup>+</sup>, 1), 432 (19), 389 (100), 371 (3) 293 (1), 259 (2), 223 (6), 165 (5), 103 (4), 75 (5). Anal. Calcd for C<sub>30</sub>H<sub>36</sub>OSi: C, 81.76; H, 8.23. Found: C, 81.61; H, 8.03.

**General synthetic procedure for molecular rotors with the protected trityl stators, exemplified by 1,4-bis[(3,3,-diphenyl-3-(3'-*tri*-isopropylsilyloxy)-phenyl)-prop-1-yn-1-yl]benzene (**1**).**

A mixture of alkyne [(3-*tri*-isopropylsilyloxy)phenyl]3,3,-diphenyl-propyne **7** (0.30 g, 0.7 mmol), 1,4-diiodobenzene (0.11 g, 0.3 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 g, 0.03 mmol), CuI (0.01 g, 0.07 mmol) and (*i*Pr)<sub>2</sub>NH (0.5 ml) in THF (25 ml) previously degassed was refluxed for 2.5 h under N<sub>2</sub> atmosphere. After this time, the reaction was cooled down to room temperature and quenched with saturated NH<sub>4</sub>Cl. The organic phase was extracted twice with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic portions were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed at reduced pressure followed for purification by column chromatography on neutral alumina, eluting with hexane/ethyl ether (99:1) afforded molecular rotor **1** as a crystalline solid (0.25 g, 77%). Melting point: 166-168 °C. FTIR-ATR ( $\nu$ , cm<sup>-1</sup>): 3061, 2944, 2866, 1596, 1485, 1446, 1385, 1277, 1182, 1142, 1073, 1002, 988, 881, 787, 765, 698, 640, 509, 458. <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.49 (2H, s), 7.39-7.29 (10H, m), 7.22 (1H, t,  $J$  = 8.4 Hz), 6.98 (1H, d,  $J$  = 8.0 Hz), 6.88-6.80 (2H, m), 1.22-1.09 (3H, m), 1.05

(18H, d,  $J$  = 6.0 Hz). <sup>13</sup>C-NMR (67.9 MHz, CDCl<sub>3</sub>)  $\delta$ : 156.0, 146.6, 145.4, 131.6, 129.3, 129.1, 128.1, 127.0, 123.3, 122.0, 121.2, 118.8, 97.4, 84.7, 56.2, 18.0, 12.7. <sup>29</sup>Si-NMR (53.67 MHz, CDCl<sub>3</sub>)  $\delta$ : 16.00. HRMS (APCI-TOF), Calcd for C<sub>66</sub>H<sub>75</sub>O<sub>2</sub>Si<sub>2</sub> 955.5300. Found: 955.5301. Error 0.09 ppm. Anal. Calcd for C<sub>66</sub>H<sub>74</sub>O<sub>2</sub>Si<sub>2</sub>: C, 82.97; H, 7.81. Found: C, 82.64, H, 7.69.

**1,4-bis[(3,3,-diphenyl-3-(3'-*tri*-isopropylsilyloxy)-phenyl)-prop-1-yn-1-yl]benzene-*d*<sub>4</sub> (**1-d<sub>4</sub>**).**

Alkyne [(3-*tri*-isopropylsilyloxy)phenyl]3,3,-diphenyl-propyne **7** (0.12 g, 0.30 mmol), 1,4-diiodobenzene-*d*<sub>4</sub> (0.45 g, 0.10 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.01 g, 0.01 mmol), CuI (0.005 g, 0.03 mmol) and (*i*Pr)<sub>2</sub>NH (0.5 ml) in THF (25 ml) previously degassed were refluxed for 8 h under N<sub>2</sub> atmosphere. Purification by column chromatography on silica gel, eluting with hexane/ethyl ether (99:1) afforded molecular rotor **1-d<sub>4</sub>** as a white crystalline solid (0.11 g, 82 %). Melting point: 166-168 °C. FTIR-ATR ( $\nu$ , cm<sup>-1</sup>): 2944, 2866, 2367, 1596, 1483, 1443, 1283, 1184, 1133, 989, 921, 881, 760, 697, 647, 574, 564. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.35-7.23 (20 H, m), 7.17 (2 t,  $J$  = 8.3 Hz), 6.92 (2H, d,  $J$  = 7.9 Hz), 6.83-6.79 (4H, m), 1.14-1.06 (6H, m), 1.00 (36 H, d,  $J$  = 6.1 Hz). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 155.9, 146.6, 145.3, 131.2 (t,  $J_{C-D}$  = 26 Hz), 129.3, 129.0, 128.1, 127.0, 123.1, 122.0, 121.2, 118.8, 97.4, 84.7, 56.1, 18.0, 12.7. <sup>29</sup>Si-NMR (99.36 MHz, CDCl<sub>3</sub>)  $\delta$ : 16.12. HRMS (APCI-TOF), Calcd for C<sub>66</sub>H<sub>71</sub>D<sub>4</sub>O<sub>2</sub>Si<sub>2</sub> 959.5613. Found: 959.5661. Error 0.9859 ppm. Anal. Calcd for C<sub>66</sub>H<sub>70</sub>D<sub>4</sub>O<sub>2</sub>Si<sub>2</sub>: C, 82.62; H, 8.19. Found: C, 81.71; H, 7.41.

**1,4-bis[(3,3,-diphenyl-3-(3'-*tri*-isopropylsilyloxy)-phenyl)-prop-1-yn-1-yl]-2,3-difluorobenzene (**2**).**

Alkyne [(3-*tri*-isopropylsilyloxy)phenyl]3,3,-diphenyl-propyne **7** (0.17 g, 0.3 mmol), 2,3-difluoro-1,4-diiodobenzene (0.07 g, 0.10 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 g, 0.01 mmol), CuI (0.01 g, 0.03 mmol) and (*i*Pr)<sub>2</sub>NH (0.5 ml) in THF (25 ml) previously degassed were refluxed for 8 h under N<sub>2</sub> atmosphere. Purification by column chromatography on silica gel, eluting with hexane/ethyl ether (99:1) afforded molecular rotor **2** as a white crystalline solid (0.11 g, 82 %). Melting point: 132-133 °C. FTIR-ATR ( $\nu$ , cm<sup>-1</sup>): 3063, 3029, 2945, 2892, 2866, 2233, 1595, 1578, 1474, 1446, 1433, 1281, 1260, 1235, 1146, 1003, 990, 876, 761, 696, 683, 639. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.33-7.24 (22H, m), 7.20 (2H, d,  $J$  = 7.9 Hz), 7.16 (2H, d,  $J$  = 2.6 Hz), 6.94 (2H, dd,  $J$  = 7.9, 1.0 Hz), 6.82 (2H, dd,  $J$  = 7.5, 2.7 Hz), 6.79-6.76 (2H, m), 1.18-1.09 (6H, m), 1.00 (36H, d,  $J$  = 6.1Hz). <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>)  $\delta$ : 155.9, 151.4 (dd,  $J$  = 14.5, 254.8 Hz), 146.0, 144.7, 129.2, 129.1, 128.2, 127.4, 127.1, 122.0, 121.1, 118.9, 114.1 ( $J$  = 7.2 Hz), 84.1, 77.4, 56.4, 17.9, 12.6. <sup>29</sup>Si-NMR (53.67 MHz, CDCl<sub>3</sub>)  $\delta$ : 16.23 ppm. <sup>19</sup>F-NMR  $\delta$ : -400.66 ppm. HRMS (APCI-TOF), Calcd for C<sub>66</sub>H<sub>73</sub>F<sub>2</sub>O<sub>2</sub>Si<sub>2</sub> 991.5113 Found: 991.5111. Error 0.13 ppm. Anal. Calcd for: C<sub>66</sub>H<sub>73</sub>F<sub>2</sub>O<sub>2</sub>Si<sub>2</sub>: C, 79.65; H, 7.32. Found: C, 79.96; H, 7.035.

**2,5-bis[(3,3,-diphenyl-3-(3'-*tri*-isopropylsilyloxy)-phenyl)-prop-1-yn-1-yl]pyridine (**3**).**

Alkyne [(3-*tri*-isopropylsilyloxy)phenyl]3,3,-diphenyl-propyne **7** (0.16 g, 0.40 mmol), 2,5-dibromopyridine (0.43 g, 0.20 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 g, 0.02 mmol), CuI (0.01 g, 0.04 mmol) and (*i*Pr)<sub>2</sub>NH (0.5 ml) in THF (25 ml) previously degassed was refluxed for 2 h under N<sub>2</sub> atmosphere. Purification by column chromatography on neutral alumina, eluting with hexane/ethyl ether (99:1) afforded molecular rotor **3** as colorless oil (0.14 g, 51 %).

%). FTIR-ATR film ( $\nu$ ,  $\text{cm}^{-1}$ ): 3027, 2238, 1951, 1809, 1595, 1581, 1539, 1489, 1467, 1445, 1362, 1270, 1180, 1064, 1030, 982, 852, 773, 690, 660.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.66 (1H, d,  $J = 2.8$  Hz), 7.76 (1H, dd,  $J = 8.4, 2.8$  Hz), 7.35 (1H, d,  $J = 8.4$  Hz), 7.32-7.26 (10H, m), 7.19 (1H, t,  $J = 8.3$  Hz), 7.01 (1H, d,  $J = 8.3$  Hz), 6.81 (1H, dd,  $J = 8.3, 2.6$  Hz), 6.71 (1H, t,  $J = 2.5$  Hz), 1.15-1.04 (3H, m), 0.99 (18H, d,  $J = 6.0$  Hz).  $^{13}\text{C-NMR}$  (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$ : 155.9, 151.2, 146.0, 144.7, 142.2, 138.8, 135.6, 129.3, 128.4, 128.2, 127.1, 122.1, 120.0, 118.9, 97.1, 83.8, 56.1, 18.0, 12.7.  $^{29}\text{Si-NMR}$  (53.67 MHz,  $\text{CDCl}_3$ )  $\delta$ : 16.20. HRMS (APCI-TOF), Calcd for  $\text{C}_{65}\text{H}_{74}\text{NO}_2\text{Si}_2$  959.5613. Found: 959.5661. Error 1.9 ppm. Anal. Calcd for  $\text{C}_{65}\text{H}_{73}\text{NO}_2\text{Si}_2$ : C, 81.62; H, 7.69; N, 1.46. Found: C, 81.80; H, 7.83; N, 1.90.

#### General synthetic procedure for the deprotection reaction exemplified with 1,4-bis-(((3-hydroxy-diphenyl)-phenylmethyl)-ethynyl)-phenylene (4).

Compound **1** (0.13 g, 0.14 mmol) and tetrabutylammonium fluoride hydrate (0.06 g, 0.20 mmol) were stirred in THF (50 mL) for 0.5 h. The resulting solid was filtered off and washed with water. The organic phase was extracted twice with  $\text{CH}_2\text{Cl}_2$  (80 ml). The organic portions were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , evaporated to dryness and purified by column chromatography on silica gel, using hexane/ethyl ether (7:3) as eluent, to afford **4** (0.08 g, 88 %). Melting point: 250-252 °C. FTIR-ATR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3429, 3059, 2930, 2228, 1598, 1491, 1448, 1260, 1223, 1031, 842, 755, 699.  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.43 (2H, s), 7.34-7.20 (10H, m), 7.16 (1H, t,  $J = 7.9$  Hz), 6.86-6.70 (3H, m), 5.60 (1H, s).  $^{13}\text{C-NMR}$  (67.9 MHz,  $\text{CDCl}_3$ )  $\delta$ : 158.2, 147.5, 146.1, 132.5, 130.0, 129.9, 129.0, 127.9, 124.2, 121.2, 117.2, 114.9, 98.3, 85.6, 57.0. HRMS (APCI-TOF), Calcd for  $\text{C}_{48}\text{H}_{35}\text{O}_2$  643.2631. Found: 643.2623. Error 1.33 ppm. MS (DIP)  $m/z$ : 643 ( $[\text{M}^+ + 1, 52]$ ), 642 ( $[\text{M}^+, 100]$ ), 565 (23), 360 (21), 359 (49), 283 (47), 281 (59), 265 (43), 252 (20); Anal. Calcd for  $\text{C}_{48}\text{H}_{34}\text{O}_2$ : C, 89.69; H, 5.33. Found: C, 89.36; H, 5.90.

#### 1,4-bis-(((3-hydroxy-diphenyl)-phenylmethyl)-ethynyl)-2,3-difluorobenzene (5).

Compound **2** (0.02 g, 0.02 mmol), tetrabutylammonium fluoride hydrate (0.01 g, 0.03 mmol) and THF (10 ml). Purification on silica gel afforded **5** as a white crystalline solid (0.01 g, 88 %). Melting point: 270-272 °C. FTIR-ATR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3359, 2928, 2867, 1611, 1500, 1450, 1287, 1237, 1052, 1017, 870, 819, 623, 570.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.32 (s), 7.31 (s), 7.29-7.26 (m), 7.18 (t,  $J = 8.0$  Hz), 7.15 (d,  $J = 2.0$  Hz), 6.87 (d,  $J = 8.0$  Hz), 6.78 (t,  $J = 2.0$  Hz), 6.76 (dd,  $J = 2.0, 8.0$  Hz).  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 155.5, 151.4 (dd,  $J = 254.8, 14.9$  Hz), 150.4, 146.6, 144.5, 129.4, 129.2, 128.2, 127.4, 127.2, 121.9, 116.4, 114.2, 103.5, 77.6, 56.4, 31.1.  $^{19}\text{F-NMR}$   $\delta$ : -400.62 ppm, HRMS (APCI-TOF), Calcd for  $\text{C}_{48}\text{H}_{33}\text{F}_2\text{O}_2$  679.2443. Found 679.2449. Error 0.93 ppm. Anal. Calcd for  $\text{C}_{48}\text{H}_{32}\text{F}_2\text{O}_2$ : C, 84.94; H, 4.75. Found: C, 85.13; H, 5.04.

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#### Notes and references

‡ The rotator of 2,3-difluoro-1,4-diiodobenzene was obtained modifying a described procedure. Colourless needles (5.3 g, 70 %). Melting point (hexanes): 52-54 °C.  $^1\text{H-NMR}$  [400 MHz,  $\text{CDCl}_3$ ] ( $\delta$ , ppm): 7.25 (m 2H).  $^{13}\text{C-NMR}$  [100 MHz,  $\text{CDCl}_3$ ] ( $\delta$ , ppm): 150.3 (dd,  $J = 250, 20$  Hz), 135.1, 82.5. T. Ruasis, M. Schlosser, *Eur. J. Org. Chem.*, 2002, **19**, 3351.

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