

# Oscillating Emission of [2]Rotaxane Driven by Chemical Fuel

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**Supporting Information** 

**ABSTRACT:** A molecular shuttle consisting of a dibenzo-24-crown-8 macrocycle and an axle with two degenerate peripheral triazolium stations, a central dibenzyl ammonium station, and two anthracenes stoppers was exposed to 2-cyano-2-phenylpropanoic acid as a chemical fuel. Protonation/deprotonation of the amine reversibly switches the rotaxane from a static and little emissive to a dynamic fluorescent shuttling device, the latter exhibiting rapid motion (15 kHz at 25 °C). Four fuel cycles were run.



T he fascinating arena of mechanically interlocked molecular machines,<sup>1</sup> such as rotaxanes<sup>2</sup> and catenanes,<sup>3</sup> has received distinct recognition with the 2016 Nobel Prize in Chemistry.<sup>4</sup> Among these systems, [2]rotaxane-based molecular shuttles, with either nondegenerate or degenerate stations, have been intensely studied.<sup>5</sup> Whereas nondegenerate molecular shuttles are widely explored as bistate switches,<sup>1c,2b,6</sup> systems with two identical binding sites, i.e., degenerate molecular shuttles,<sup>7</sup> are less known.<sup>8</sup> For some rigid [2]-rotaxanes, the thermal shuttling of the macrocycle has been shown to be independent of the distance between the degenerate stations.<sup>8a</sup> Further insight into the dynamic effects of shuttling is thus needed for improving nanoscaled devices, e.g., those used in molecular electronics.<sup>9</sup>

Herein we present a switchable [2]rotaxane<sup>10</sup> in which the degenerate shuttling is switched "ON" and "OFF" by addition of the chemical fuel, 2-cyano-2-phenylpropanoic acid (1), developed by Di Stefano et al.<sup>11</sup> Switching by chemical fuel has lately gained momentum.<sup>12</sup> Usually, switching between two states requires the sequential addition of a forward and backward stimulus, like acid–base,<sup>13</sup> reductant–oxidant,<sup>14</sup> irradiation–heating,<sup>15</sup> or light at two different wavelengths.<sup>16</sup> Due to its unique features, the chemical fuel 1 acts first as acid and after decarboxylation as strong base. Starting with **R-2**, fuel 1 should first generate **R-1** (Figure 1) that does not show any shuttling motion. Deprotonation of **R-1** yields **R-2** exhibiting rapid shuttling ( $k_{298} = 15$  kHz), which changes the electronic properties at both triazolium stations. In contrast to static fluorescence switches,<sup>17</sup> cyclic emission is now possible.

In order to prepare the dynamic molecular shuttle **R-2**, we resorted to the switchable rotaxane motif developed by Coutrot et al.<sup>18</sup> Traditionally, the stations in rotaxanes are linked by long alkyl chains, but for the present work we synthesized the [2]rotaxane **R-1** with two degenerate triazolium stations connected via a short dibenzylammonium bridge (see the Supporting Information). Terminal anthracenes were used both as stoppers and fluorescence probes. The triazolium methylene



**Figure 1.** Chemical structure and cartoon representation of molecular shuttles. Intense blue color indicates strong fluorescence of anthracene units and light color indicates weak fluorescence.

anthracene unit was utilized recently by Li et al. for reversible switching in a [2]rotaxane resulting in two different fluorescent states.<sup>19</sup>

In rotaxane R-1 (Figure 1), the macrocycle has a stronger affinity toward the ammonium moiety than toward the triazolium units. Thus, it preferentially sits on the central station without visible shuttling. Using DBU and TFA as the external stimuli, switching between R-1 and R-2 is highly reversible, as demonstrated from <sup>1</sup>H NMR and fluorescence spectroscopic data. When R-1 is deprotonated with DBU,

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significant changes are observed in the <sup>1</sup>H NMR indicative of formation of **R-2**. The occurrence of a single set of triazolium proton signals at 25 °C suggests rapid shuttling of the macrocycle between both triazolium units (vide infra). Protons 1-H and 16-H (methyl protons) of the triazolium rings exhibit an upfield shift from 8.75 to 8.56 ppm and from 4.09 to 3.05 ppm, respectively (Figure 2A). On the other hand, protons 8-H



Figure 2. (A) Partial <sup>1</sup>H NMR spectra (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) (a) of R-1, (b) after addition of 1 equiv of DBU to R-1 (generating R-2), and (c) after addition of 1 equiv of TFA (regenerating R-1). (B) Switching fluorescence reversibly by toggling between R-1 and R-2 ( $\lambda_{exc} = 252 \text{ nm}, 10^{-5} \text{ M}$ ) in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C.

and 9-H are shifted downfield, while all anthracene stopper protons display upfield shifts owing to shielding effects by the crown-ether ring. These <sup>1</sup>H NMR shifts clearly indicate complexation between the crown ether and the triazolium rings. Upon protonation with TFA the macrocycle returns back to the ammonium site; see the <sup>1</sup>H NMR spectra in Figure 2A.

As shown in Figure 2B, both rotaxanes R-1 and R-2 exhibit typical anthracene emission patterns but at quite different intensity. In R-1, fluorescence is almost quenched due to a strong PET from the excited anthracene to the triazolium units.<sup>19</sup> When 1 equiv of base was added to afford R-2, the emission intensity immediately increased ca. 10-fold (Figure 2B). Apparently, association of the macrocycle with the triazolium rings fully or partly prevents quenching by PET. Addition of 1 equiv of acid to R-2 decreases the fluorescence intensity again to the original value. Therefore, the switching can readily be monitored by means of either <sup>1</sup>H NMR or luminescence spectroscopy.

Inspiration to use a chemical fuel has come from the report by Di Stefano in which acid 1 undergoes protonation, smooth decarboxylation, and proton back transfer in the presence of an acid–base switchable catenane at room temperature.<sup>11a</sup> Similarly, we use acid 1 as a chemical fuel to drive the switchable molecular shuttle. Addition of 100 mol % of acid 1 to rotaxane **R-2** in  $CD_2Cl_2$  causes a drastic change in the <sup>1</sup>H NMR within a few seconds with concomitant formation of **R-1**. Reformation of **R-2** is observed in about 9 min following the steps depicted in Figure 3.

To investigate the fuel-driven reversible cycle between R-2 and R-1, we started from rotaxane R-2. After addition of an



**Figure 3.** Dynamic interconversion of states B–D of rotaxane R-2 (= starting state B) fueled by 2-cyano 2-phenylpropanoic acid (1).

equimolar amount of acid 1, the <sup>1</sup>H NMR recorded after 45 s revealed a mixture of rotaxanes R-1 and R-2 in a ratio of 2:3 (see Figure S26). After 9 min (Figure 4), all proton signals



**Figure 4.** Partial <sup>1</sup>H NMR spectra  $(CD_2Cl_2, 25 \ ^{\circ}C)$  recorded after mixing equimolar amounts of rotaxane **R-2** ( $c = 1.5 \ ^{\circ}M$ ) and acid 1 at various times (after start). Marked signals are assigned to protons using the following symbols: O, rotaxane **R-1**;  $\blacktriangle$ , rotaxane **R-2**; \*, benzyl proton of compound 4.

corresponding to **R-1** had disappeared. A new parallel signal at 3.94 ppm increasingly emerged that is characteristic for the benzylic proton of 4. Finally, full back transformation of **R-1** into **R-2** is clearly proven by the appearance of all **R-2** peaks with original intensity.

Following the fuel-driven transformation ( $c = 10^{-5}$  M,  $CH_2Cl_2$ ) by fluorescence spectrometry revealed additional insight. As indicated in Figure 2B, rotaxane R-1 exhibits low and rotaxane R-2 ca. 10-fold increased fluorescence intensity. After the chemical fuel 1 had been added to the solution of R-2, spectra were measured in 1 min intervals (Figure 5B and Figures S40 and S41). Right after addition, the fluorescence intensity decreased drastically within the first minute. As the low fluorescence intensity of state A is not reached, the protonation of R-2 by acid 1 apparently furnishes a mixture of R-1 and R-2 (calculated as 3:1: state C). Over the course of ca. 25 min, the fluorescence intensity increases constantly (state C  $\rightarrow$  D). The concentration dependence of the recovery toward state D indicates that not only decarboxylation but also final deprotonation of R-1 contribute to the overall rate. In the course of four fueled cycles, each ignited by addition of 1 equiv of acid 1 (Figure 5C), the fluorescence drops rapidly after each addition and recuperates over ca. the same time, but never to the original level as defined by state B (Figure 5B). With increasing cycles, a slight decrease of both the high-level and low-level emission intensity is visible that most likely finds an



**Figure 5.** Four cycles of the shuttling of **R-2** upon addition of fuel **1**. (A) Photographs of one oscillation cycle. (B) First cycle. (C) Fluorescence intensity changes at 421 nm vs time ( $\lambda_{exc} = 252 \text{ nm}$ ,  $c = 10^{-5} \text{ M}$ ) in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C over four cycles.

explanation in the fuel byproducts that absorb at the excitation wavelength ( $\lambda_{\text{exc}} = 252 \text{ nm}$ ).

In order to investigate the translational oscillation in shuttle **R-2**, the <sup>1</sup>H VT-NMR<sup>20</sup> was analyzed. At room temperature, rotaxane **R-2** exhibits the <sup>1</sup>H NMR spectrum of a compound with 2-fold symmetry, as it shows only one set of proton signals for the triazolium stations and anthracene stoppers. The proton signals of 1-H and 16-H (of the triazolium groups) appear as broad singlets at 8.56 and 3.05 ppm, respectively. Upon lowering the temperature, the singlet corresponding to proton 1-H broadens almost to baseline at 0 °C (see Figure S28). Lowering the temperature further, the signal first disappears and then reappears near -30 °C. The emergence of two very broad peaks indicates that now the symmetry is broken. As the temperature is further decreased, the signals of proton 1-H develop into two sharp singlets with equal intensity (Figure 6)



Figure 6. Experimental (left) and simulated (right) partial VT  $^{1}$ H NMR spectra (CD<sub>2</sub>Cl<sub>2</sub>, 600 MHz) of **R-2** shows the splitting of the signal of proton 1-H (magenta asterisk).

at 9.10 and 8.70 ppm (at -75 °C). The signal at 8.70 ppm corresponds to proton 1-H<sub>UC</sub> (UC = uncomplexed) as it matches with that of proton 1-H in rotaxane **R-1** (8.75 ppm) (Figure 2A). The initial distinct downfield shift of the triazolium proton 1-H<sub>C</sub> (C = complexed) may be attributed to hydrogen bonding between 1-H<sub>C</sub> and the oxygen atoms of DB24C8 in a restricted arrangement.<sup>21</sup> The slight upfield shift of proton 1-H<sub>C</sub> in the temperature range -30 to -75 °C may be explained by slowing the rotational dynamics of the crown

(around its own central axis) increasing partial shielding of the triazolium unit via both benzene rings of the macrocycle. The signal of proton 1-H at 8.56 ppm was simulated with the aid of WINDNMR<sup>22</sup> allowing the determination of the exchange frequency k at various temperatures. At 25 °C the exchange frequency  $k_{298}$  was calculated to be 15 kHz. The activation parameters obtained for the dynamic process in **R-2** are  $\Delta H^{\ddagger} = 31.3 \text{ kJ mol}^{-1}$ ,  $\Delta S^{\ddagger} = -60.0 \text{ J mol}^{-1} \text{ K}^{-1}$ , while the free energy barrier at 25 °C was calculated to be 49.2 kJ mol<sup>-1</sup>.

To get some insight into the effect of shuttling on the photophysical properties, we performed fluorescence studies for both **R-1** and **R-2** in dichloromethane from +25 to -75 °C. In both cases, the emission wavelength did not alter, indicating that the fluorescing state remains the same. In **R-1**, where shuttling is restricted, the fluorescence intensity continuously increased as expected from the well-known temperature effect.<sup>23</sup> However, in the dynamic rotaxane **R-2** the fluorescence remained roughly constant from +25 to -20 °C. Only, below -20 °C it increased as expected by the temperature effect (Figure 7). This unforeseen behavior



Figure 7. Variable-temperature normalized fluorescence intensity of R-1 and R-2 monitored at 421 nm ( $\lambda_{exc} = 252$  nm,  $1 \times 10^{-5}$  M) in CH<sub>2</sub>Cl<sub>2</sub>.

deserves a comment. In the low-temperature regime (-20 to -75 °C), the macrocycle is located on one of the triazole units and thus prevents PET quenching at this site. In return, the other triazolium unit behaves as in **R-1** triggering strong PET quenching of the nearby anthracene luminescence. This kinetically slow system acts like a normal fluorophore, reflecting the temperature effect.

In contrast, the constant fluorescence intensity (from +25 to -20 °C) may be associated with the fast oscillating dynamics of the ring between the triazolium stations. As there is no increase of fluorescence, the slowing of the ring oscillation between +25 and -20 °C that should be associated with a decrease of fluorescence apparently is more or less counterbalanced by the inherent temperature effect on fluorescence, which should lead to increased emission intensity upon lowering the temperature.

In conclusion, we have synthesized a switchable molecular [2]rotaxane that is static and hardly emissive in the protonated state and a luminescent oscillating shuttle after deprotonation. The kinetic parameters obtained from variable-temperature <sup>1</sup>H NMR indicate an exchange frequency of 15 kHz at 25 °C. Moreover, the shuttling motion is reversibly and dynamically switched "ON" and "OFF" by the iterative addition of the chemical fuel **1**, as observed by both <sup>1</sup>H NMR and fluorescence

spectroscopy. Notably, the shuttling has particular temperature effects on the luminescence.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.7b03996.

Synthetic procedures and full spectral characterization of all new compounds, fueled reaction cycles, and fluorescence studies (PDF)

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Synthesis, characterization, steady-state fluorescence, and VT-NMR studies by A.G. Low-temperature fluorescence studies by M.A. and C.W.

## Notes

The authors declare no competing financial interest.

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