



## Two functional [2]rotaxanes featuring efficient intercomponent interactions between chromophores



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### ABSTRACT

Two functional [2]rotaxanes, with a 4-morpholin-naphthalimide fluorophore as one of the two stoppers and a difluoroboradiaza-*s*-indacene functionalized dibenzo[24]crown-8 as macrocycle, were designed, synthesized and well characterized. [2]Rotaxane **1** and **2** had almost the same structural skeleton, and a ferrocene unit was introduced in [2]rotaxane **1** as the other stopper, while a 3,5-dimethoxybenzene stopper in [2]rotaxane **2**. It has shown that efficient energy transfer process in both two [2]rotaxanes occurred from the 4-morpholin-naphthalimide donor to the difluoroboradiaza-*s*-indacene acceptor. Moreover, [2]rotaxane **1** exhibited a remarkable fluorescence increase in response to the addition of base that can drive the shuttling motion because of the introduction of ferrocene electron donor. This work can pave the way for the design and construction of complex and functional molecular systems based on the mechanically interlocked molecules.

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### 1. Introduction

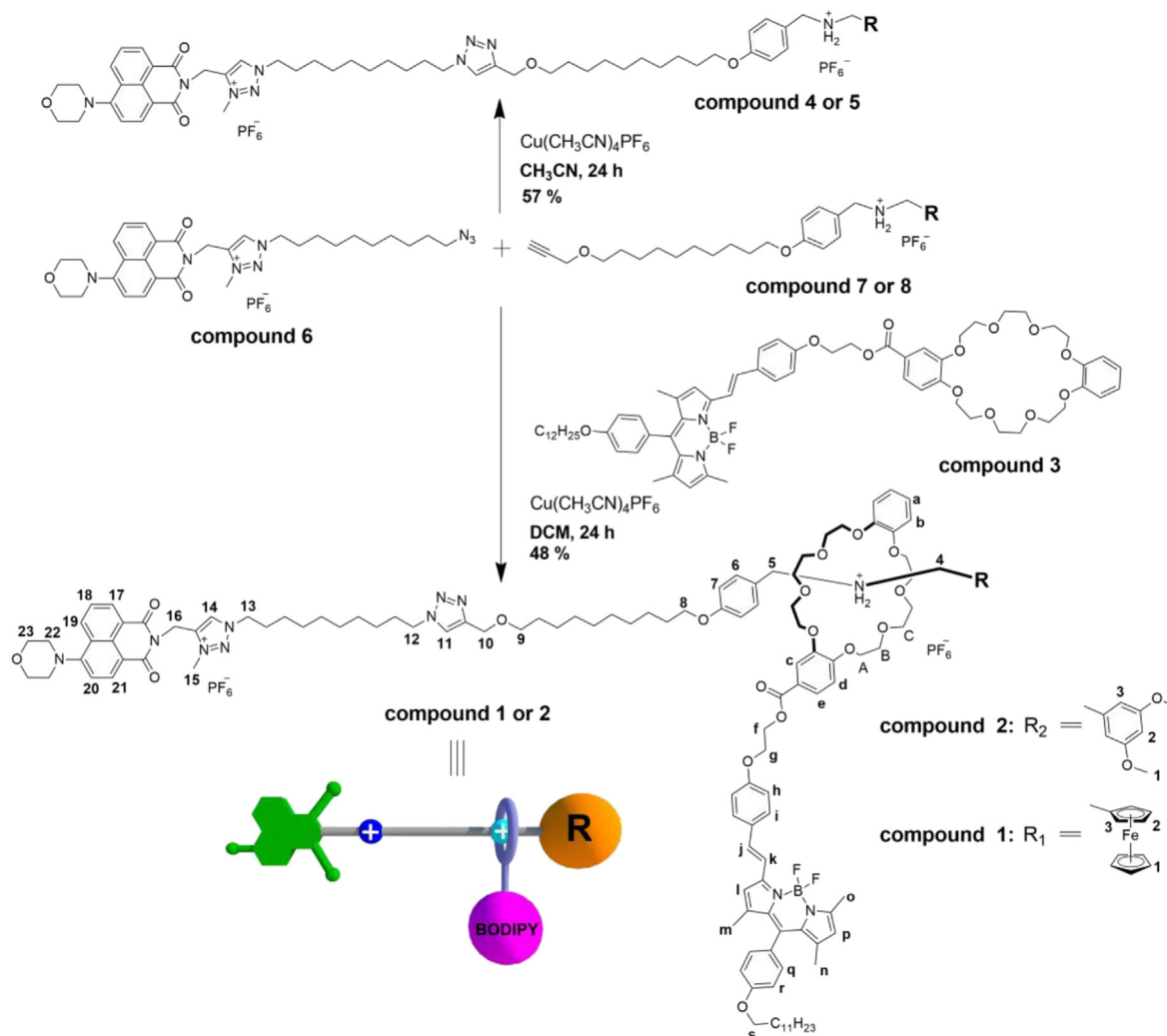
Molecular machines have captured great interests of chemist and biologist not only because of their controllable, reversible, and readable properties, but also their potential applications in the creation of nanometer-scale molecular devices [1–5]. Mechanically interlocked molecules (MIMs), in particular rotaxanes and catenanes, have attracted a great deal of attentions in the design of molecular machines because their components can move reversibly between two or more stations under the influence of various external stimuli, and these assemblies are of enormous significance for the construction of nanometer-scale molecular devices [6–16]. Bistable [2]rotaxanes, one of the most common species of MIMs, in which a macrocycle was interlocked onto a dumbbell-shaped component and switched between two distinct, well-separated recognition sites on the thread component in response to external stimuli, have been developed and extensively studied because of their efficient synthesis and controllable properties [17–23]. In some cases, the relative movement of the constituent parts of [2]rotaxanes can dramatically change the photophysical or electrical properties of molecules without any structural change in the fluorophore itself [24–28], which makes them one of the best

candidates for the construction of molecular switches or molecular logic gates [29–31]. Meanwhile, by introducing photo- or electro-active units on the axle or the ring component, [2]rotaxanes can achieve specific functions and realize intercomponent interactions such as electron transfer [32–36], energy transfer [37–39], charge transfer interactions [40–42].

In our previous work [43], we have reported a *bis*-branched [3] rotaxane that contains two chromophoric units, namely, an oligo(*para*-phenylenevinylene) (OPV) in the middle of the axis unit and two BODIPY(difluoroboradiaza-*s*-indacene) dyes in two dibenzo[24]crown-8 (DB24C8) rings, in which efficient energy transfer process from the central OPV chromophore to outer BODIPY chromophores was observed. In order to increase functional complexity, in this paper, two functional [2]rotaxanes with chromophores were designed, prepared, and investigated. As shown in Scheme 1, each of rotaxanes employed a 4-morpholin-naphthalimide (**MA**) fluorophore as one stopper in the rod, and a BODIPY-functionalized DB24C8 as macrocycle. Both two rotaxanes contained two distinguishable stations for dibenzo[24]crown-8 (**DB24C8**) ring, namely, a dibenzylammonium (**DBA**) [44–48] and an *N*-methyltriazolium (**MTA**) [49–53] recognition sites, which were separated by two long alkyl chains. A functional ferrocene (Fc) unit was introduced in [2]rotaxane **1** as another stopper. Owing to the large overlap between the emission spectrum of 4-morpholin-naphthalimide (**MA**) fluorophore and the absorption spectrum of BODIPY fluorophore, efficient energy transfer from the **MA**

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**Scheme 1.** The synthetic routes for the preparation of [2]rotaxane **1**, **2**, dumbbell compounds **4**, **5** and key intermediate compound **3**.

fluorophore on the axle to the BODIPY fluorophore on the DB24C8 macrocycle happened. In addition, the BODIPY-functionalized DB24C8 macrocycle in the [2]rotaxanes can also reversibly shuttle between two distinguishable recognition sites in response to external acid-base stimuli. Furthermore, in [2]rotaxane **1**, the fluorescence of the BODIPY fluorophore increased in response to the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), in which a weaker efficient distance-dependent photoinduced electron transfer (PET) process [54–56] that occurs between the ferrocene (Fc) electron donors and the excited BODIPY fluorophore was involved.

## 2. Experiment

### 2.1. General information

All chemicals were obtained commercially and used as received unless otherwise mentioned.  $^1\text{H}$  NMR spectra were recorded at 400 MHz and  $^{13}\text{C}$  NMR spectra were recorded at 100 MHz using  $\text{CD}_3\text{COCD}_3$  or  $\text{DMSO}-d_6$  as a solvent and tetramethylsilane as an internal standard. All mass spectrometric analyses were performed on ThermoStar™ mass spectrometer. Absorption and fluorescence spectra were recorded on a Varian Cary 100 and a Varian Cary Eclipse using quartz cuvette at room temperature, respectively.

### 2.2. Synthesis

#### 2.2.1. Synthesis of compound 7

A mixture of **9** (1.00 g, 3.15 mmol) and **10** (0.809 g, 3.78 mmol) in dry toluene (30 mL) was refluxed overnight under nitrogen atmosphere. Then the solvent was removed under vacuum, and the residue was dissolved in MeOH (30 mL).  $\text{NaBH}_4$  (0.599 g, 15.75 mmol) was added to the solution in ice bath. After the mixture was stirred overnight, the solution was poured into water, and extracted by dichloromethane ( $3 \times 50$  mL). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then concentrated in vacuo. The residue was dissolved in MeOH (20 mL) and HCl (6 M, 1 mL) was added in ice bath. Then the mixture was stirred for 2 h at room temperature. After the solvent was removed under vacuum, the residue was redissolved in MeOH (30 mL), and then saturated  $\text{NH}_4\text{PF}_6$  (15 mL) was added. After the mixture was stirred for 4 h, the mixture was washed by water (30 mL) and extracted by DCM ( $3 \times 50$  mL). The organic layer was dried over anhydrous sodium sulfate and then concentrated. The residue was purified by chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$ : MeOH (100: 1) as eluent to get compound **7** (1.56 g, 75%) as a gray solid.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  = 8.74 (s, 2H), 7.35 (d,  $J$  = 8.4 Hz, 2H), 6.97 (d,  $J$  = 8.4 Hz, 2H), 4.39 (m, 2H), 4.27 (m, 2H), 4.21 (m, 5H), 4.08 (d,  $J$  = 2.4 Hz, 2H), 4.02–3.93 (m, 6H), 3.43–3.38 (m, 3H), 1.73–1.65 (m,

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