



A mechano-responsive molecule with tricolored switch



Zhiyong Ma^a, Zhijian Wang^a, Yan Li^{b,*}, Sicheng Song^a, Xinru Jia^{a,*}

^a Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

^b College of Science, Hebei University of Engineering, Handan, China

ARTICLE INFO

Article history:

Received 26 August 2016

Revised 19 October 2016

Accepted 22 October 2016

Available online 24 October 2016

Keywords:

Mechanochromic

Rhodamine 6G

Anthracene

Ring-opening reaction

Tricolored switch

ABSTRACT

We herein report the mechanical force induced reversible tricolored switch of a single organic molecule **M-2**. It was constructed with two chromophores of an anthracene unit and a rhodamine 6G moiety bridged through an oligopeptide of tetraphenylalanine. The multicolored switch of this molecule is from the synergetic effect of two mechanisms of supermolecular structure change and chemical structure alteration. The different π - π overlapping interactions of neighboring anthracene rings and the ring-opening reaction of rhodamine 6G lead to the switch of three colors of bluish green, blue and yellow.

© 2016 Elsevier Ltd. All rights reserved.

Introduction

Modulating luminescent properties of solid materials with mechanical energy is a fascinating subject, because the mechanical-responsive materials show various applications as sensors, memory devices and security systems [1,2]. More importantly, the mechanical stimulus represents a reliable power source available in our daily life for the chemical [3–5] and physical transformations of luminescent materials [6–8]. Up to now, numerous molecules with mechanically induced luminescent color change have been documented in the literatures. The relationship between the molecular structures and the luminescent properties has also been discussed [9–14]. However, the design concept for mechano-responsive materials is still obscure. Moreover, the materials with two colors change are usually observed [15–21], but the multicolor changed materials are yet scarce [22–27]. Hence, it is highly indispensable to develop fundamental design strategies for the rational synthesis of molecules with desirable properties, especially for the molecular materials with multicolored switch upon force-stimuli.

We are interested in the design of molecules with multicolored emission from the combination of self-assembled structure transformation and chemical reactions [28–31]. Our molecular design strategy is to incorporate two chromophores in a single molecule, such affording the materials with novel mechanochromic proper-

ties via different emission mechanisms. That is “one molecule, two mechanisms and three colours” [32,33]. We previously reported the force-induced tricoloured switch of a single organic molecule (**M-1**) with two chromophores of a pyrene group and a rhodamine B unit in the structure [29]. The aim for this work is focused on the verification of our molecular design strategy for tricolor switchable mechanochromic molecules. For exploring its applicability and advancing our knowledge to deeply understand the relationship between molecular structures and mechanochromic properties, we designed and synthesized the molecule **M-2**. **M-2** was constructed from two chromophores of an anthracene and a rhodamine 6G, which differed from **M-1** with the chromophores of pyrene and rhodamine B although the two systems were quite similar. Compared with **M-1**, **M-2** could gel in THF/ethyl acetate at room temperature. Its xerogel sample exhibited the interesting mechanochromic switching properties. A blue-shift was observed after slightly grinding, which is molecular structure dependent because the bulky and twisted rhodamine 6G moiety blocked the π - π overlapping of anthracene rings and such effect was enhanced by the external force. It is worth mentioning that **M-2** is a rarely reported example that a blue-shift was observed upon grinding.

Results and discussion

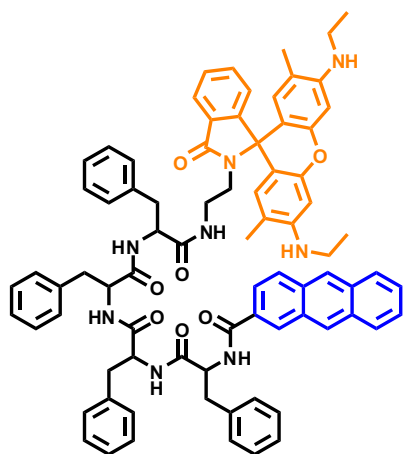
M-2 was synthesized from rhodamine 6G (the ring-opened form) which reacted with ethylenediamine to afford Rh6G-NH₂ (the spiro lactam form); then a standard DCC coupling of Rh6G

* Corresponding authors.

E-mail address: xrjia@pku.edu.cn (X. Jia).

and Boc-protected PHE-PHE output compound **1**; compound **2** was obtained as a white powder by repeating a two-reaction cycle, namely, removing the Boc group of **1** by trifluoroacetic acid and triethylamine, and then linking the resultant intermediate to the Boc-protected PHE-PHE; finally, the designed molecule **M-2** was produced via the reaction of Boc-deprotected **2** with Anthracene-2-carboxylic acid. **Scheme 1** shows the structure of **M-2** containing a spacer of four phenylalanine residues, an anthracene moiety and a rhodamine 6G unit. ^1H NMR, ^{13}C NMR and HR-MS measurements were used to verify the structure and purity of **M-2** (Figs. S1 and S2). The detailed synthetic procedures and characterizations of **M-2** are described in the Supporting Information (Scheme S1).

M-2 gelled in THF/ethyl acetate at room temperature. After evaporating the solvent slowly, a xerogel sample was obtained as a solid piece with the interesting mechanochromic properties. The as-prepared xerogel sample emitted at 465 nm; it showed a



Scheme 1. Molecular structure of **M-2**.

blue-shift with the wavelength at 460 nm along with a new peak at 437 nm after slightly grinding. With further force disturbance, these two peaks merged and centered at 440 nm, meanwhile, a new emission at 557 nm appeared as a tag of the yellow powder (Fig. 1). The color change was partly reversible. We observed the fluorescent emission reappearance at 440 nm when heating the yellow powder on a temperature-controlled heating stage at 150 °C for 10 min (Fig. S3).

As reported in the literature, the emission of anthracene closely depends on the π - π overlapping degree of the aromatic rings. That means the emission colors of anthracene dependent on the molecular arrangement. It is convinced that the green color emission implies the stronger interchromophore interaction of anthracene rings, while the less overlapped neighboring anthracene rings lead to blue or bluish-green colors. In addition, anthracene can form three types of excimers based on the geometry of the individual anthracene unit in the excited state. One is stable excimer that emits at 470 nm with two anthracene units overlapped each other with an angle of 55°. The other one is sandwich-type excimer with the emission maximum at about 560 nm. While the third one is T-shaped excimer with the wavelength at 510 nm [34].

In our case, we suppose that the original xerogel was composed of anthracene dimers with the stronger interaction of aromatic rings, possibly corresponding to the stable excimer with two anthracene units mostly overlapping packed. However, the interaction of some adjacent anthracene rings was reduced because of the slippage of them upon slightly grinding. With further force action, most of the aromatic rings slipped to a less overlapped mode with the emission blue-shifted to 437 nm. The continuous grinding initiated the ring-opening reaction of rhodamine 6G from a spirolactam to a ring opened amide, leading to the powder with yellow color. We speculate that the blue-shifted emission is molecular structure dependence. The bulky and twisted rhodamine 6G moiety blocks the π - π overlapping of anthracene rings and such effect is enhanced by the external force. The blue-shifted emission is rarely reported in the mechanochromic study. We previously

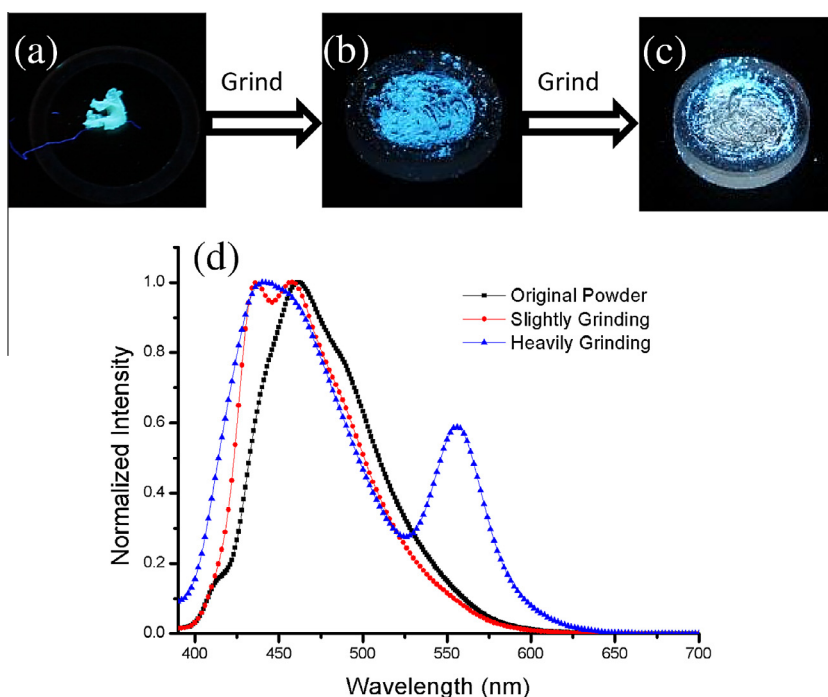


Figure 1. Optical images of (a) original bluish-green powder; (b) blue powder after slightly grinding; (c) yellow powder after continuous grinding; (d) fluorescence spectra of the initial powder and the same sample upon grinding ($\lambda_{\text{ex}} = 365$ nm).

Download English Version:

<https://daneshyari.com/en/article/5265879>

Download Persian Version:

<https://daneshyari.com/article/5265879>

[Daneshyari.com](https://daneshyari.com)