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An acid/base responsive side-chain polyrotaxane system with a fluorescent signal

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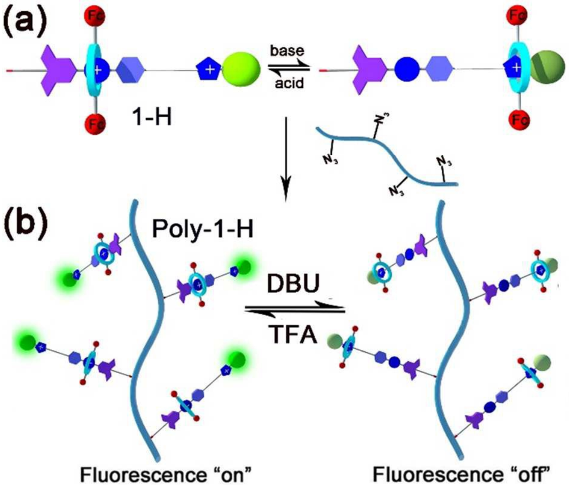
An acid/base-responsive polyrotaxane system was constructed, in which the side chain was modified with a diferrocene-functionalized bistable rotaxane molecular switch *via* "CuAAC" click reaction. The reversible subunit shuttling movement of the rotaxane unit in the polymer system in response to external acid/base stimuli was accompanied with visual fluorescence changes.

Mechanically interlocked molecules (MIMs), well known as rotaxanes and catenanes,[1] have gained considerable attention in past decades due to their unique capability of mimicking the behaviours in biological systems.[2] The introduction of various functional groups into the structure of MIMs can lead to the formation of functional MIMs, in many cases, the corresponding properties can be switched reversibly and controllably, such as novel molecular switches.[3] Many types of functional MIMs, especially bistable rotaxanes, have been reported , in which rotaxanes can be employed as nanovalves,[4] switchable catalysts,[5] molecular pumps,[6] fluorescent switches,[7] molecular logic gates,[8] etc. These elegant fabrications vitally advance the evolution of rotaxanes.

Following the great success in the study of rotaxanes in homogeneous solution, a promising strategy to realize further functional applications is interfacing these rotaxane molecules with other polymeric structures or solid nanostructures.[9] Some advances have been presented recently in the rotaxane-based self-assembled monolayers with switchable ability in wettability,[10] catalytic activity,[11] aggregation of nanoparticles,[12] etc. Very recently, we reported the successful immobilization of a previously reported typical [2]rotaxane fluorescent switch (Scheme 1a) onto the surface of silica nanoparticles,[13] indicating the promising potential as a novel solid-state fluorescent switch. Given the significant role of polymer as the platform supporting the functional molecules, as shown in many previous reports,[14] we expected the integration between fluorescence-switchable rotaxane and polymer to breed a novel type of polymer-supporting rotaxane fluorescent switch. Here we present the successful modification of the typical fluorescence-switchable bistable [2]rotaxane **1-H** onto the side chains of linear polymers through "CuAAC" click reaction,[15] resulting in a novel polyrotaxane **Poly-1-H** (Scheme 1b). The reversible subunit shuttling movement of polymer system in response to external acid/base stimuli was accompanied with visual fluorescence changes. This work is expected as a promising step forward to the functionalization of [2]rotaxane fluorescent switches.



Scheme 1. Schematic representation of (a) the relative shuttling movement of the rotaxane-type fluorescent switch in response to external acid–base stimuli and (b) immobilization of this rotaxane onto azide-modified linear polymer and its switching on polymer chain responding to external acid/base stimuli.

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In our precious report, we designed and synthesized an alkyne-terminated bistable [2]rotaxane molecular switch **1-H** which introduces two ferrocene (Fc) moieties as electron donors in the dibenzo[24]crown-8 (DB24C8) macrocycle,[7] where the uniform relative mechanical movement of macrocycle component between two different stations was driven by external acid–base stimuli accompanied by obvious visual fluorescence changes (Scheme 1a). Utilizing the similar strategy, azide-modified linear polymer (**Poly-N$_3$** shown in Fig. 1) was expected to be able to covalently bind with alkyne-terminated [2]rotaxane **1-H**. The polymer main chain was prepared by reversible addition fragmentation chain transfer (RAFT) reaction between 6-azidohexyl methacrylate **2** and butyl methacrylate **3** in DMF at 70 °C, resulting in a line poly(6-azidohexyl methacrylate and butyl methacrylate) (**Poly-N$_3$**) with a Mn of 10.05 kDa and a PDI of 1.39 and a yield about 83 %. The copolymerization ratio of m/n was calculated as 1/30 according to the integration ratios of ^{1}H NMR signals of **Poly-N$_3$**. Significantly, it should be noted that additional alkyl chain was employed as the "background" of the side chain by integrating the monomer **2** with the other monomer **3**. The highly diluted concentration of side-chain azide groups ensured enough space for the efficient shuttling of the bound [2]rotaxane.[16] Following the efficient "CuAAC" reaction between polymer **Poly-N$_3$** and alkyne-terminated [2]rotaxane **1-H**, rotaxane modified polymer **Poly-1-H** can be obtained with a yield about 67 % after washing with methanol for several times and then dialysis against DMF and ethanol for three days, ensuring all the unreacted compound **1-H** and catalyst Cu(CH$_3$CN)$_4$PF$_6$ was removed completely. As a result, the side-chain polyrotaxane **Poly-1-H** was obtained with a Mn of 21.35 kDa and a PDI of 1.36.

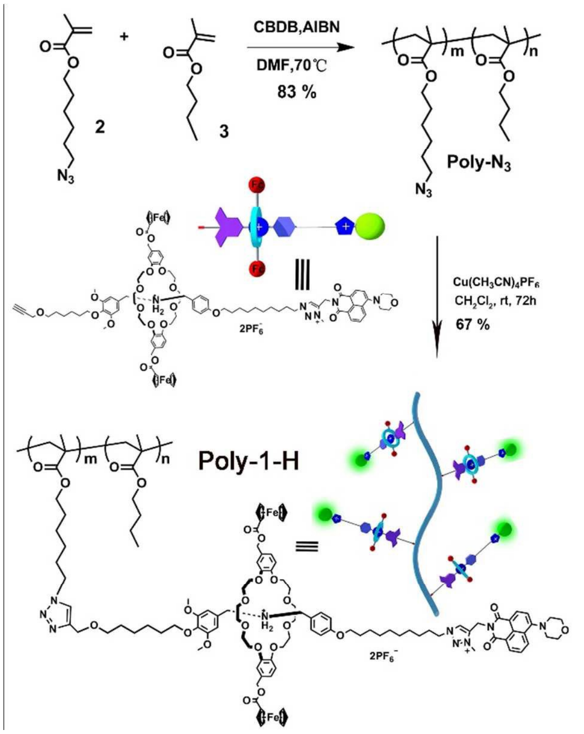

Figure 1. The synthesis of the **Poly-N$_3$** and polyrotaxane **Poly-1-H**.

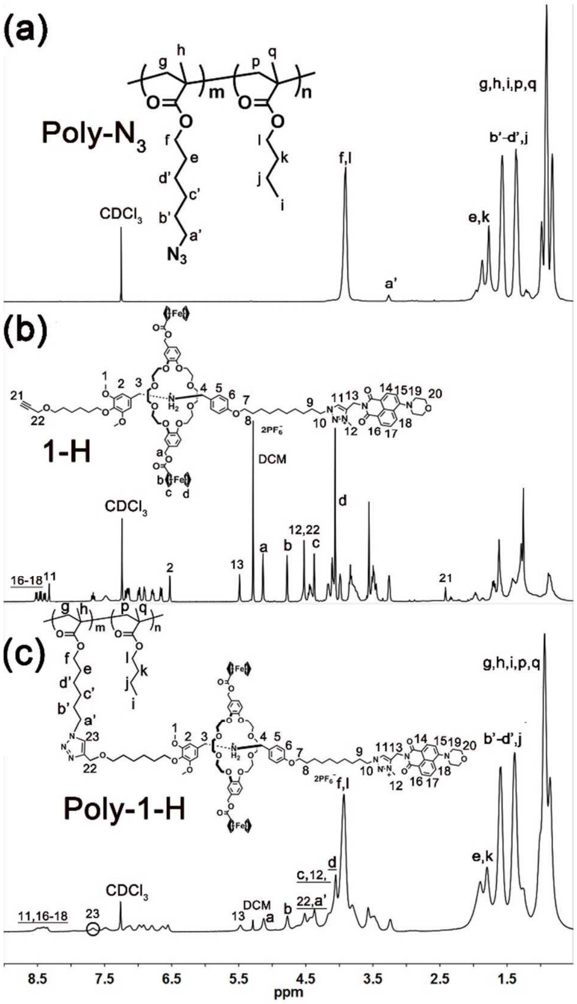

Figure 2. ^{1}H NMR spectra (400 MHz, CDCl$_3$, 298 K) of **Poly-N$_3$** (a), [2]rotaxane **1-H** (b) and polyrotaxane **Poly-1-H** (c), the black circle in the bottom indicates the presence of the triazole proton 23.

The key intermediate **Poly-N$_3$** and the target polyrotaxane **Poly-1-H** were characterized by ^{1}H NMR and FT-IR spectra as discussed below. In the ^{1}H NMR spectrum of **Poly-N$_3$** (Figure 2a) , the signals of the methylene groups next to the azide group and the ester group were obvious at 3.28 ppm (H$_{a'}$) and 3.93 ppm (H$_f$, H$_l$), respectively. In addition, the signals of the polymeric methylene groups (H$_e$, H$_k$, H$_{b'}$, H$_{d'}$, H$_j$) at 1.30 ppm to 2.06 ppm and the methyl groups (H$_g$, H$_h$, H$_i$, H$_p$, H$_q$) from 0.75 ppm to 1.10 ppm could be observed. What's more, the FT-IR spectrum of **Poly-N$_3$** indicting the presence of the azide functional group at 2096 cm^{-1} and the carbonyl group at 1728 cm^{-1} (Figure 3a).[17] The ^{1}H NMR of compound **1-H** in CDCl$_3$ had been particularly characterized. As shown in Figure 2b, the proton H$_{11}$ on MTA station site was located at 8.35 ppm and the proton H$_{12,}$ H$_{13}$ neighboring MTA station site were located at 4.53 ppm, 5.50 ppm, respectively. And the proton H$_{21}$ of alkyne group was located at 2.42 ppm. In addition, the proton H$_a$, H$_b$, H$_c$ and H$_d$ on DB24C8 macrocycle could also be observed.

After the click reaction between **Poly-N_3** and compound **1-H,** using $Cu(CH_3CN)_4PF_6$ as catalyst and dichloromethane as solvent, there were several obvious changes in ^1H NMR spectrum and FT-IR spectrum. Firstly, in the ^1H NMR spectrum of **Poly-1-H** (Figure 2c), the disappearance of peak of 2.42 ppm and the emergence of peak of 7.67 ppm indicating the disappearance of alkyne group (H_{21}) and the appearance of the new triazole proton H_{23}. Secondly, the azidomethylene signal shifted from 3.28 ppm to 4.37 ppm (peak a') and the other particular protons peak of **Poly-N_3** and compound **1-H** could be observed in the ^1H NMR spectrum of the **Poly-1-H** as well instead of which were a series of broad peaks**.** Thirdly, the FR-IR spectrum of **Poly-1-H** (Figure 3b) witnessed the total disappearance of the azide group peak at 2096 cm^{-1},[17] while the carbonyl group peak at 1728 cm^{-1} remains unchanged demonstrating high reaction efficiency. All the evidence supported the fact that the compound **1-H** was modified onto the polymer successfully and our expected target polyrotaxane **Poly-1-H** had been obtained.

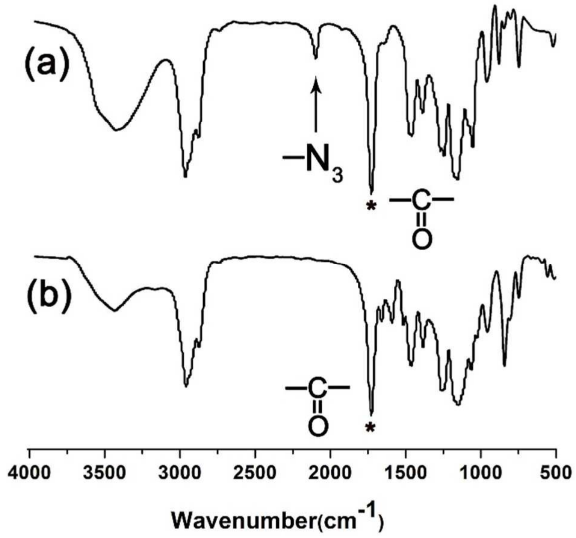

Figure 3. FT-IR spectra of **Poly-N_3** (a) and polyrotaxane **Poly-1-H** (b).

Now that the reversible translocation movement of the macrocycle between the DBA and MTA recognition sites in [2]rotaxane **1-H** was particular characterised by ^1H NMR spectroscopy and the photophysical properties of [2]rotaxane **1-H** had been already studied in our previous work.[13] Then we discussed the photophysical properties of polyrotaxane **Poly-1-H**. The **Poly-1-H** exhibited a strong absorption peak at λ_{max} = 410 nm in its UV-Vis spectra (Figure S3) and an apparent typical emission peak at λ_{max} = 521 nm in CH_2Cl_2 solution (Figure 4a), which was in agreement with the properties of MA fluorophore and further proved that compound **1-H** was modified onto the polymeric structure successfully. After adding excess DBU to the CH_2Cl_2 solution of **Poly-1-H**, there was no obvious change in UV-Vis spectra (Figure S3), while the fluorescence spectrum intensity decreased 80% compared to its original state (Figure 4a). This phenomenon could be explained to a closer distance between the ferrocene-functionalized DB24C8 macrocycle and MA fluorophore upon the addition of DBU. As a result, the PET process occurred between the electron-rich Fc units and the electron-deficient MA fluorophore. After addition excess TFA to the DBU-added CH_2Cl_2 solution of **Poly-1-H,** the UV-Vis spectra still unchanged while the fluorescence intensity recovered to its original state. This may be explained by the DB24C8 mocrocycle returned to its initial site after the re-protonation of the DBA station. Scanning electron micrography (SEM) was used to observe the microstructure of the polyrotaxane **Poly-1-H**. Figure S4 shows the porous 3D structure of **Poly-1-H**, indicating the formation of polymerized network because of the aggregation of polymer chain via noncovalent interactions. At last, the confocal fluorescence microscopy (CFM) was carried out to observe the fluorescence properties of **Poly-1-H** before and after adding DBU (Figure 4b). All these consequences confirmed that we had successfully constructed a fluorescent switch based on a polyrotaxane system, which could realize the relative shuttling motion in response to external stimuli.

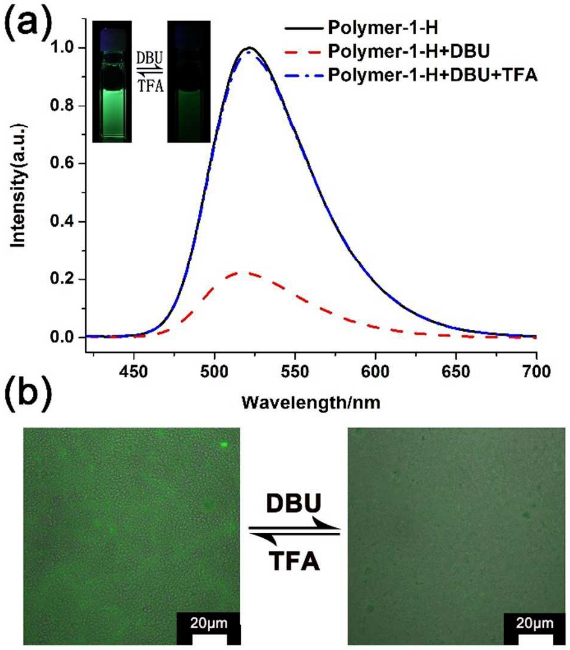

Figure 4. (a) Normalized fluorescence spectral changes in CH_2Cl_2 solution of **Poly-1-H** (0.5 mg/ml), the mixture obtained after adding excess DBU to the solution of **Poly-1-H** and the mixture obtained after adding excess TFA to the DBU-added solution of **Poly-1-H.** (b) Confocal fluorescence micrographs of solid-state **Poly-1-H** before and after addition of excess DBU. The excitation wavelength was 410 nm.

Conclusions

In conclusion, we have successfully constructed a bisable [2]rotaxane-modified polymer with switchable fluorescence. The relative shuttling movement of the system in response to external stimuli was accompanied by visual fluorescence changes due to the change of PET process. The shuttling motion could be realized in solution of polymer structures. Utilizing polymer as a platform supporting the efficient working of [2]rotaxane fluorescent switch, this system expands the application fields of MIMs and is expected to be potential in applications including smart stimuli-responsive materials and solid-state fluorescent sensors.

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A side-chain polyrotaxane system can generate a remarkable fluorescent signal change in response to acid/base stimulus.