

Abstract

Synthesis of Naphthalimide Derivative and Diketopyrrolopyrrole (DPP)-Based [2]Rotaxane/Polyrotaxane as Novel Chemosensor Materials and a Controllable Hierarchical Nano Self-Assembled Structure from Polyrotaxane

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The pivotal objective of this dissertation is to construct novel orthogonally H-bonded mechanically interlocked molecular/polyrotaxane architectures with an asymmetric (Diketopyrrolopyrrole) stopper and to study their molecular shuttling process under solvent, anion, and acid-base stimuli control along with their controllable hierarchical nanostructure formations plugged with positive cooperativity non-covalent interactions. In the introduction of this doctoral thesis we have introduced brief early synthetic attempts to create mechanically interlocked molecules (MIMs) such as rotaxanes and catenanes as well as their polymeric counterparts. Moreover novel templating methodologies to build MIMs and some latest examples of MIMs based molecular shuttles under various stimuli control were also introduced. Fundamentally, underplayed chemo sensing mechanisms in these systems were presented. Meanwhile, we have developed a novel and facile fluorescent ratiometric chemodosimeter for grisly toxic hydrazine via mild Ing-Manske phthalimide deprotection method in this doctoral thesis as well.

In chapter two, a novel [2]rotaxane based on an orthogonal H-bonded motif and 3,6-di(thiophenyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (**DPP**) with controlled topicity was successfully constructed, displaying excellent stimulated responses toward anion and solvent polarity. The extensive ¹H & ¹⁹F NMR titrations were lucidly revealed the binding site and the mode binding interaction as well. The preorganized host selectively recognized F⁻ with high optical sensitivity and reversibility via enhanced positive cooperativity and noncovalent interaction by evidence of a shorter fluorescence lifetime. Therefore we developed a first prototype [2]rotaxane molecular shuttle for selective recognition of F⁻ with high optical outputs.

In chapter three, four analogous polymers were systematically synthesized by copolymerization of a 9-alkylidene-9*H*-fluorene monomer with various monomers, which contained a diketopyrrolopyrrole unit tethered with a dumbbell unit, a metalated [2]rotaxane, a demetalated orthogonal H-bonded [2]rotaxane, and a simple alkyl chain, to furnish **P1**, **P2**, **P3**, and **P4**, respectively, to investigate the supramolecular interactions of the mechanically interlocked rotaxane pendants and conjugated polymer backbones. Prevailing ¹H NMR and UV-vis to NIR titration profiles indicated that the novel polyrotaxane **P3** showed a sensitive and reversible acid-base molecular switch capability via supramolecular interactions in contrast to the other polymers (**P1**, **P2**, and **P3**). Compared with the other polymers, **P3** possessed a narrower bandgap, which was also confirmed by the computational study. Prominently, the monitoring of a controllable nano-self-assembly process of **P3** was obtained by reversible acid-base molecular switch approaches. The orthogonal H-bonded pendant [2]rotaxane unit and the steric demand of **P3** judiciously allowed to morph into a hierarchical nanostructure via interconvertible H-bonds, anion- π and π - π stackings, as well as hydrophobic interactions.

In chapter four, A facile and sensitive fluorescent probe for hydrazine based on phthalimide appended hydrophilic naphthalimide was successfully constructed, displaying excellent colorimetric and ratiometric responses towards hydrazine via Ing-Manske phthalimide deprotection conditions in semi-aqueous buffer solution. The estimated detection limit was as low as 4.2 nM (hydrazine content = 1 ppb) far below than the threshold limit value (TLV) of 10 ppb according to the U. S. Environmental Protection Agency (EPA). Prevailing detection of hydrazine in living cells of the current probe is demonstrated.

Thus in conclusion, a novel archetype **DPP** based highly fluorescent [2]rotaxane was developed. The remarkable stimulated responses towards solvent polarity and fluoride ion were discussed. Moreover, the extended efforts of this current design into polyrotaxane architectures along with their acid-base controllable hierarchical nanostructure formations via reversible optical molecular switch approaches coupled with various non-covalent interactions were discussed. Furthermore a novel fluorescent ratiometric chemodosimeter for hydrazine based on Ing-Manske phthalimide deprotection was presented in detail.

Chinese Abstract

合成 Naphthalimide 衍生物與含 Diketopyrrolopyrrole (DPP) 為基底之 [2]Rotaxane/Polyrotaxane 作為新穎化學感測材料及可操控規則奈米自組裝結構之 Polyrotaxane

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本論文的主要目標是合成新的正交氫鍵機械互鎖/聚輪烷分子不對稱結構（二酮吡咯並吡咯）塞，並研究其在溶劑條件、陰離子及酸鹼刺激下控制分子的穿梭過程並调控其納米結構的形成插入正協同非共價相互作用。在本博士論文中，我們已經簡短介紹了早期嘗試合成如輪烷和索煙及其聚合物機械互鎖分子（MIMS）。此外，我們介紹了新穎的模板方法合成 MIMS 和一些最新的例子基於 MIM 的分子梭在各種環境刺激下控制。從根本上來說，在這些系統裡化學感測正在被運用。同時，在這個博士論文中我們已開發出一種新型和淺顯的螢光比例來測定有毒胂並透過緩和的 Ing-Manske 鄰苯二甲酰亞胺去保護的方法。

在第二章中，成功建構一種新型的[2]輪烷的基礎上正交氫鍵和 3,6 - 二（噻吩基）吡咯並 [3,4-C]吡咯-1,4 (2*H*,5*H*) - 二酮 (DPP) 與控制 topology，表現出對陰離子和溶劑極性優異的刺激反應。廣泛的運用 ^1H 和 ^{19}F NMR 滴定顯示出的結合位點和模式以及結合相互作用。其中證明了 preorganized 會選擇性地確認 F-光靈敏度高和可逆性通過增強的正協同和非共價相互作用的螢光壽命較短。因此，我們開發出了新型的選擇性氟離子光學[2]輪烷的分子開關。

在第三章中，四個類似的系統合成聚合物共聚單體與各種單體，含有二酮吡咯並吡咯單元與啞鈴單元拴，金屬化[2]輪烷，demetalated 的正交氫鍵 9 亞-9*H*-芴[2]輪烷，和一個簡單的烷基鏈，透過 **P1**, **P2**, **P3** 和 **P4**, 分別研究的機械聯鎖的輪烷的垂飾和共軛聚合物骨架的超分子相互作用機制。運用 ^1H NMR 和紫外可見近紅外滴定的檔案證明了新型聚輪烷 DM RTP 通過對比其他聚合物 (**P1**, **P2** 和 **P3**) 本身是一個敏感的且在酸鹼溶液下分子開關能力為可逆的超分子相互作用。**P3** 與其他聚合物相比，具有更窄的帶隙，這也經過計算研究證實了。特別的是，一個可控的納米自組裝過程 **P3** 的監測可藉由可逆酸鹼分子開關的方法來驗證。正交氫鍵垂飾[2]輪烷單元可以變形到一個納米次結構並藉由相互轉換的 H-bond，陰離子- π 和 π - π stackings，以及疏水性相互作用。

在第四章，成功的合成胂苯二甲酰亞胺附加親水 naphthalimide，顯示出優異的色度和比例對胂的反應，通過 Ing-Manske 鄰苯二甲酰亞胺半水緩衝溶液中去保護條件是一種簡便和敏感

的螢光探測。估計檢測限低至 4.2 nM (卍含量= 1 ppb) 根據美國環境保護署 (EPA)，遠遠低於閾值限值 (TLV) 為 10 ppb。證明卍電流對於活細胞檢測的可行性。

因此，一種新型的基於 archetype **DPP** 高螢光[2]輪烷的開發。討論了溶劑極性和氟離子的刺激的反應。此外，該電流的設計隨著酸鹼調控的層次加上透過可逆的光學分子開關的方法，以及各種非共價相互作用的納米結構形成的聚輪烷的體系結構擴展進行了多方討論。此外，對於 Ing-Manske 鄰苯二甲酰亞胺脫卍一種新型的螢光比例 chemodosimeter 做了詳細介紹。



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