

Communication

Rotaxane Based on Bis-Porphyrin Threaded onto Bis-Viologen Macrocycle

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ABSTRACT: Rotaxanes have been prepared using benzene-linked bis-porphyrin or bis-zinc porphyrin as a string component and bis-viologen as a macrocyclic ring component. Absorption and fluorescence spectra of rotaxanes formed by complexation of two components have been investigated.

Construction of some interlocked molecules, such as pseudorotaxanes, rotaxanes, and catenanes may be considered as one of the most useful tools for preparing the functional synthetic molecular-level nanomachines or switches.¹⁻¹¹ When the proper chemical or physical stimuli are used, their interlocked structures allow tunable translational motion at the nanoscale. The mechanical movements of movable components from the stationary components in molecular machine may be induced in response to some external stimulus such as pH, chemical, electrical energy, or light. In turn, some observable properties such as absorption or luminescence are switched on/off and thereby opening up the way to process information at the molecular level.

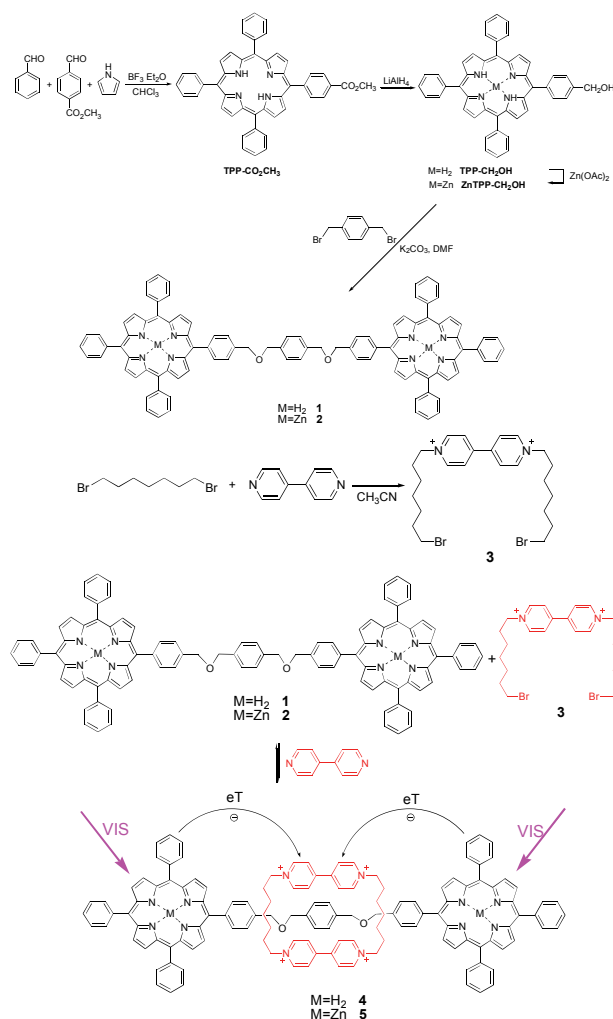
Rotaxanes¹² consisting of ring and string fragments have been very accessible compounds by the many efficient template synthesis studied since 1980s. The template-directed synthetic strategies reliant on pi-electron donor-acceptor interactions, transition metal complexation, and steric fit/hydrogen bonding have not only made the synthesis of rotaxanes more accessible but have also allowed the preparation of compounds incorporating chemically, electrochemically, and photochemically accessible functionalities. They play a role as building blocks for molecular-scale electronic and photonic devices. Recently, a wide variety of rotaxanes with different strings and macrocyclic rings have been developed for different applications.

Among external stimuli activating the molecular machine, light has many advantages such as no generation of waste products, rapid on/off switching, and easy monitoring.¹³ In terms of building light-controllable molecular machine, it is interesting to introduce photo-active components such as porphyrin and viologen into the supramolecular interlocked molecules including rotaxanes.

Porphyrins are strong visible light absorbing molecules and frequently employed as electron donor in multicomponent electron transfer systems. Benzene is used as a linker as well as a typical π -electron donor. Positively charged viologen is a typical electron acceptor. Moreover, many positively charged rotaxanes have been prepared by self-assembly through π -stacked interaction between viologen and aromatic compound.¹⁴⁻¹⁶

In supramolecule composed of porphyrin and viologen or other electron acceptor, it is expected that visible irradiation leads to the generation of excited porphyrin and then photoinduced electron transfer from excited porphyrin to viologen or other electron acceptor.^{17,18} Light-induced redox reaction of viologen moiety may apply to derive the light-triggered translocation of molecular components in rotaxanes.¹⁹ While many rotaxanes²⁰ and pseudorotaxanes²¹ containing both porphyrin and viologen have been studied, rotaxanes consisting of porphyrin string and viologen macrocycle has not been reported yet.

In this study, light-active rotaxanes consisting of porphyrin-benzene-porphyrin or zinc porphyrin-benzene-zinc porphyrin, as a string component, threaded with bis-viologen, as a macrocyclic ring component, have been prepared and their absorption and fluorescence spectral properties have been investigated.



Scheme 1. Synthetic Procedure of Rotaxanes 4 and 5.

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Scheme 1 describes synthetic procedure of rotaxanes **4** and **5**.

5-(Methyl-4-benzoate)-10,15,20-triphenylporphyrin (TPP-CO₂CH₃) was prepared by stirring the 3:1:4 mixture of benzaldehyde, methyl 4-formyl benzoate, and pyrrole in chloroform with BF₃·Et₂O, according to the reported procedure.²²⁻²⁴ TPP-CO₂CH₃ was reduced to 5-(4-hydroxymethylphenyl)-10,15,20-triphenylporphyrin (TPP-CH₂OH) with the addition of LiAlH₄ in freshly distilled tetrahydrofuran.²³ Zinc 5-(4-bromomethylphenyl)-10,15,20-triphenylporphyrin (ZnTPP-CH₂OH) was obtained by stirring vigorously the solution of TPP-CH₂OH with excess zinc acetate in the mixed solvent (9/1, v/v) of dichloromethane and methanol.²³ Porphyrin-benzene-porphyrin **1** and zinc porphyrin-benzene-zinc porphyrin **2** were prepared in 40 and 36% yield, respectively, by stirring after the addition of potassium carbonate into the mixture of TPP-CH₂OH or ZnTPP-CH₂OH and 1,4-bis-(bromomethyl)-benzene in dimethylformamide. 1,1'-Bis(7-bromoheptyl)-4,4'-bipyridine-1,1'-dium **3** was prepared by the reaction of 4,4'-dipyridine and 1,4-bis(bromomethyl)benzene in dry acetonitrile. The structures of compounds **1** and **3** were identified using ¹H-NMR spectra.²⁵

Rotaxanes **4**²⁶ and **5** composed of bis-porphyrin or bis-zinc porphyrin threaded onto bis-viologen macrocycle were prepared by refluxing a solution of porphyrin-benzene-porphyrin **1** or zinc porphyrin-benzene-zinc porphyrin **2** and 1,1'-bis(7-bromoheptyl)-4,4'-bipyridine-1,1'-dium **3** with 4,4'-bipyridine in dry acetonitrile and purified with column chromatography (CH₂Cl₂:CH₃OH = 95:5).

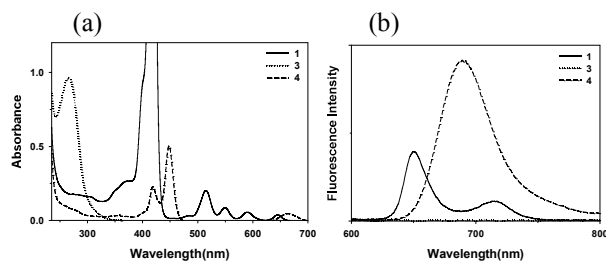


Figure 1. (a) Absorption and (b) fluorescence spectra of rotaxane **4** (10 μM) with those of **1** and **3** in dichloromethane ($\lambda_{\text{ex}}=435$ nm).

Figure 1 shows absorption and fluorescence spectra of rotaxane **4** with those of porphyrin-benzene-porphyrin **1** and viologen derivative **3** in dichloromethane. In Figure 1, absorption and fluorescence spectral features of rotaxane **4** are similar to those of diprotonated porphyrin H₂Por²⁺, where two pyrrole imine nitrogens in the core accept two protons.^{27,28} In this case, core nitrogens in rotaxane **4** may be protonated by HCl production from the porphyrin-catalyzed photodecomposition of dichloromethane.

Figure 2 shows absorption and fluorescence spectra of rotaxane **5** with those of zinc porphyrin-benzene-zinc porphyrin **2** and viologen derivative **3** in dichloromethane. In Figure 2, absorption and fluorescence spectra of rotaxane **5** are very similar to those of zinc porphyrin-benzene-zinc porphyrin **2** except substantial quenching (~36%) of fluorescence, probable due to the photoinduced electron transfer from zinc porphyrin moiety to viologen moiety.

Further detailed study for photoinduced electron transfer in rotaxanes **4** and **5** is in progress.

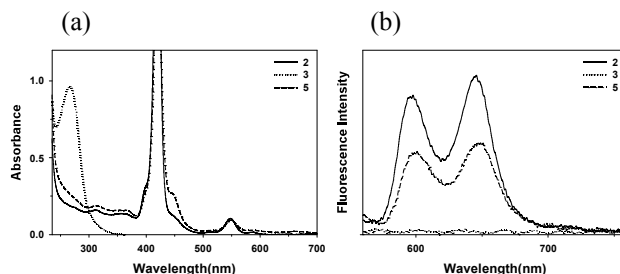


Figure 2. (a) Absorption and (b) fluorescence spectra of rotaxane **5** (10 μM) with those of **2** and **3** in dichloromethane ($\lambda_{\text{ex}}=550$ nm).

KEYWORDS: Porphyrin, viologen, rotaxane, electron transfer

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25. ¹H-NMR (400 MHz); **1**(CDCl₃): δ 8.68-8.80 (16H, m, pyrrole), .10-7.50 (42H, m, aromatic), 5.22 (8H, m, CH₂O), -2.75 (4H, broad s, pyrrole-NH). **3**(DMSO-d₆): δ 9.31-9.36 (4H, m), 8.83-8.88 (4H, m), 4.92 (4H, t), 3.30 (4H, t), 2.22 (4H, m), 1.80 (4H, m), 1.30-1.50 (12H, m).
26. **4**: yield 4%, purple solid, ¹H-NMR (400 MHz, DMSO-d₆): δ 9.31-9.36 (8H, m, pyridinium), 8.68-8.90 (24H, m, pyrrole, pyridinium), 8.10-7.50 (42H, m, aromatic), 4.90-5.22 (16H, m, CH₂O, CH₂N), 2.32 (8H, m), 1.50-1.80 (12H, m), -2.75 (4H, broad s, pyrrole-NH).
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