Journal of Metals, Materials and Minerals, Vol. 32, No. 3, pp. 60-67, 2022

Multi-responsive rotaxane with tunable fluorescence under azobenzene-based benzoxazine structure

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Received date:
15 May 2022
Revised date
15 July 2022
Accepted date:
30 July 2022

Keywords:
Rotaxane;
Benzoxazine;
Light responsiveness;
Supramolecule

Abstract

Rotaxanes are known for the mechanically interlocked molecules for decades. The present work demonstrates a method to prepare multi-responsive rotaxane by conjugating with a multi-responsive supramolecule. Benzoxazine dimers, *N, N'*-bis(3,5-dimethyl-2-hydroxybenzyl) methylamine derivatives, are good models because their simple chemistry. An azobenzene containing benzoxazine with remaining hydroxyl group for further conjugation with rotaxane was designed. The ring opening of rotaxane using fluorescent phenol provides benzoxazine dimer with metal ion responsive and fluorescent properties. Based on this concept, light responsive benzoxazine conjugated with rotaxane system shows light, metal ion and rotaxane shuttling responsiveness which can be followed by fluorescent signals. The present work shows simple way to develop rotaxanes with multi-responsive functions using supramolecular chemistry of benzoxazine dimer prepared from light responsive phenol.

1. Introduction

For the past decade, responsive materials have received much attention due to their unique properties, for example, controllable conformation, adjustable solubility and reversible molecular assembly [1-3]. The most common studies with external stimuli are temperature, light, pH, and mechanical force, which can be applicable in chemosensor, biosensor, photochromic materials, etc. A light responsive functional group which has received much attention for decades is azobenzene. Its conformation can be changed between *trans* and *cis* forms under UV light [4]. This reversibility effectively controls the physical property of materials, for example, film bending, hydrophobic-hydrophilic switching [5,6]. The conjugated bond is also recognized for light responsiveness. Under the proper conditions, conjugated molecules such as naphthalene, fluorene and etc. are known to emit fluorescent light [7,8]. Although their responsiveness is attractive, it is difficult to incorporate them to other molecules due to the complicated modification steps resulting in low yields [9].

On this viewpoint, the present work proposes azobenzene derivatives with benzoxazine molecular structures. Since benzoxazine is flexible in molecular design by simply changing phenol to azobenzene phenol, the azobenzene derivative with benzoxazine molecular structure can be obtained. In addition, when benzoxazine undergoes ring-opening to a benzoxazine dimer, the dimer also forms metal ion complexes. Moreover, our research group succeeded in developing benzoxazine dimer which shows inter- and intramolecular hydrogen bonding and also metal ion complexation [10-12].

Rotaxanes are mechanically interlocked compounds consisting of linear molecular guests encircled by macrocyclic hosts. In general, the linear molecules are stabilized in the macrocycles by end capping the terminals with bulky groups. Various classes of host molecules, such as crown-ethers, cyclodextrins, calixarenes, were reported for rotaxane fabrication. The self-assembled pseudorotaxane can be applied for reversible chain extended, star and block copolymers so called polymer topology transformations [13-17]. Polyrotaxanes are potential advanced materials such as self-healing polymers, stimuli responsive materials, molecular machines, actuators, and sensors [18]. The incorporated non-covalent interactions impact the molecular behaviors [19] such as dynamic crosslinking [20,21], tunable light responsiveness [22-27], etc.

It comes to our question whether azobenzene-based benzoxazine and aromatic-based crown ether possess any specific performances under rotaxane structure or not. In fact, the unique properties of those rotaxanes are induced by the change of the interaction between the macrocycle and the linear molecule. On this viewpoint, the use of azobenzene-based benzoxazines lead not only to molecular interaction either π-π or charge-charge but also development of fluorescence as a consequence of molecular shuttling. It can be expected that the rotaxane obtained shows the effect on fluorescence emission. The present work, for the first time, demonstrates the multi-responsiveness of rotaxanes with a benzoxazine dimer containing azobenzene.

DOI: 10.55713/jmmm.v32i3.1269

2. Experimental

2.1 Materials

Phenol, 2-naphthol, copper(II) chloride and 3-amino-1-propanol was purchased from Sigma-Aldrich Corporation. 4-Aminophenol, 3,5-dimethylbenzaldehyde, 4-aminomethylbenzoic acid, tributylphosphine ($\mathrm{Bu_3P}$), dibenzo-24-crown-8 (DB24C8), *N,N'*-dicyclohexylcarbodiimide (DCC), sodium triacetoxyborohydride ($\mathrm{NaBH(OAc)_3}$), and sodium borohydride ($\mathrm{NaBH_4}$) were purchased from Tokyo Chemical Industry Co., Ltd., Japan. Potassium hydroxide, sodium hydroxide, ammonium hexafluorophosphate ($\mathrm{NH_4PF_6}$), toluene and 1,4-dioxane were purchased from Wako Pure Chemical Industries Ltd., Japan. Paraformaldehyde, sodium nitrite, methanol, N-methyl-2-pyrrolidone (NMP), chloroform and dichloromethane were purchased from Nacalai Chemicals, Ltd., Japan. All chemicals and solvents were used as received.

2.2 Characterization

^{1}H- (500 MHz) and ^{13}C- (125 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 500 spectrometer using $\mathrm{CDCl_3}$ and DMSO-d_6 as the solvents. The spectra were referenced to tetramethylsilane as the internal standard. IR spectra were recorded on a Bruker Alpha spectrometer. Matrix-assisted laser desorption/ionization–time of flight–mass spectrometry (MALDI–TOF–MS) were recorded on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV using the linear-positive ion mode. The sample polymer solution (1 mg·mL^{-1}) was prepared in THF or $\mathrm{CHCl_3}$, and the matrix (dithranol) and cationizing agent (sodium trifluoroacetate) were dissolved in THF (10 mg and 1mg·mL^{-1}, respectively). The polymer solution and the matrix solution were mixed and deposited onto a sample target plate and allowed to dry in air at room temperature. Mass values were calibrated by the two-point method with insulin b plus Hþ at 3497.96 and R-cyanohydroxy cinnamic acid dimer plus H^+ at 379.35. Preparative GPC was performed using a HPLC LC-918 instrument from the Japan Analytical Industry equipped with a Megapak-Gel 201C. UV-VIS absorption spectra were recorded on an Agilent cary 300 UV-VIS spectrophotometer. Fluorescence spectra were recorded on a Cary Eclipse spectrofluorometer (Agilent Technologies). The UV exposure was performed in chamber using a UV lamp (RUV 533 BC) covering wavelengths from 315 nm to 400 nm.

2.3 Syntheses

2.3.1 Synthesis of azobenzene-based benzoxazine (AP-Bzx)

3-Aminopropanol (0.80 g, 10 mmol) and paraformaldehyde (0.80 g, 25 mmol) were mixed in dioxane and toluene (1:1, 30 mL) at 70°C for 1 h. The solution of 4,4'-dihydroxyazobenzene (Azo-OH) (1.09 g, 5 mmol) in dioxane (20 mL) was added. The solution temperature was increased to 110°C and kept for 6 h. After removing the solvents, the crude product was dissolved in chloroform (100 mL) and then washed with 0.5 M NaOH (100 mL) several times and then brine. The organic layer was collected and dried over an excess amount of $\mathrm{Na_2SO_4}$ until the reddish solution was clear. Then, $\mathrm{Na_2SO_4}$ was filtered, and the solvent was removed to obtain AP-Bzx. (Scheme 1A) (Yield: 75%)

^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$, 25°C): $\delta = 7.77$ (d, $J = 9$ Hz, 2H, ArH), 7.66 (s, 2H, ArH), 6.94 (d, $J = 9$ Hz, 2H, ArH), 4.36 (s, 4H, OCH_2N), 4.03 (s, 4H, NCH_2Ar), 3.88 (t, 4H, CH_2OH), 2.97 (m, 4H, NCH_2CH$_2$), 1.78 (m, 4H, CH$_2$$CH_2CH_2$). ^{13}C-NMR (125 MHz, $\mathrm{CDCl_3}$, 25°C): $\delta = 160.4$ (s, Ar-O-CH$_2$), 146.1 (s, Ar=N), 124.7 (s, Ar), 122.7 (s, Ar), 121.2 (s, Ar), 83.8 (s, NCH_2O), 67.8 (s, HO-CH_2CH$_2$), 54.9 (s, ArCH_2N), 49.2 (s, NCH_2CH$_2$), 22.3 (s, CH$_2$$CH_2CH_2$). Anal. Calcd for $\mathrm{C_{22}H_{28}N_4O_4}$: C, 64.06; H, 6.84; N, 13.58 Found: C, 65.50; H, 7.00; N, 10.67. MS (ESI/MicroTOF) m/z: $[M + H]^+$ Calcd for $\mathrm{C_{22}H_{29}N_4O_4}$ 413.2183; Found 413.2252.

2.3.2 Synthesis of 1

3,5-Dimethylbenzaldehyde (2.7 g, 20 mmol) and 4-aminomethylbenzoic acid (3.2 g, 20 mmol) were mixed in methanol (50 mL) and triethylamine (10 mL). The reaction was carried out under reflux for 6 h. The solution was filtered followed by removing the solvent to obtain 1. (Scheme 1B) (Yield: 85%)

^{1}H-NMR (400 MHz, $\mathrm{CDCl_3}$, 25°C): $\delta = 8.33$ (s, 1H, CCHN), 8.05 (d, $J = 8$ Hz, 2H, ArH), 7.40 (s, 2H, ArH), 7.34 (d, $J = 7$ Hz, 2H, ArH), 7.08 (s, 2H, ArH), 4.85 (s, 2H, NCH_2Ar), 2.35 (s, 6H, CH_3Ar)

2.3.3 Synthesis of 2 and 3

A solution of 1 (2.70 g, 10 mmol) in methanol (20 mL) was added to a $\mathrm{NaBH_4}$ solution (1.9 g, 50 mL). The reaction was allowed at room temperature for 12 h before removing the solvent. The product was dissolved in chloroform and dried under vacuum for 2 h to obtain 2. The compound 2 (2.30 g, 9 mmol) was dissolved in a small amount of methanol (2 mL) followed by 12 M HCl (2 mL). The solution obtained was poured in diethyl ether and the precipitate was collected. The product was dissolved in a small amount of methanol (2 mL) before adding a concentrated solution of $\mathrm{NH_4PF_6}$. The product was precipitated in water to obtain 3. (Yield: 75%)

^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$, 25°C): $\delta = 7.99$ (d, $J = 8.24$ Hz, 2H, ArH), 7.59 (d, $J = 8.15$ Hz, 2H, ArH), 7.07 (s, 2H, ArH), 7.05 (s, 1H, ArH), 4.23 (s, 2H, ArCH_2N), 4.08 (s, 2H, ArCH_2N), 2.28 (s, 6H, ArCH_3)

2.3.4 Synthesis of 5

The compound 3 (0.50 g, 1.2 mmol) was mixed with DB24C8 (0.64 g, 1.4 mmol) in dried dichloromethane for 15 min. DCC (0.74 g, 3.6 mmol), AP-Bzx (0.12 g, 0.3 mmol) and $\mathrm{Bu_3P}$ (2 mg, 0.01 mmol) were added to the solution. The reaction was carried out at room temperature for 48 h. The product was purified by preparative GPC to obtain 5. (Yield: 50%).

2.3.5 Ring opening reaction of 5, 6

Compound 5 (0.25 g, 0.12 mmol) was dissolved in dioxane (15 mL). Excess 2-naphthol was added to the solution. The solution was heated to 100°C and kept for 12 h to obtain crude product 6. The compound 6 was purified by column chromatography using mixture of chloroform and methanol (3:1 v/v) as mobile phase. (Yield: 70%)

2.3.6 Shuttling of 6 by methylation, 7

Compound 6 (0.10 g, 37 μmol) was mixed with paraformaldehyde (44.8 mg, 1.5 mmol), $NaBH(OAc)_3$ (79.5 mg, 0.375 mmol) and triethylamine (0.15 g, 1.5 mmol) in NMP solvent (5 mL). The reaction was carried out at 70°C for 24 h. The compound 7 was purified by preparative GPC. (Yield: 73%)

2.3.7 Metal ion complexation, ($7/Cu^{2+}$)

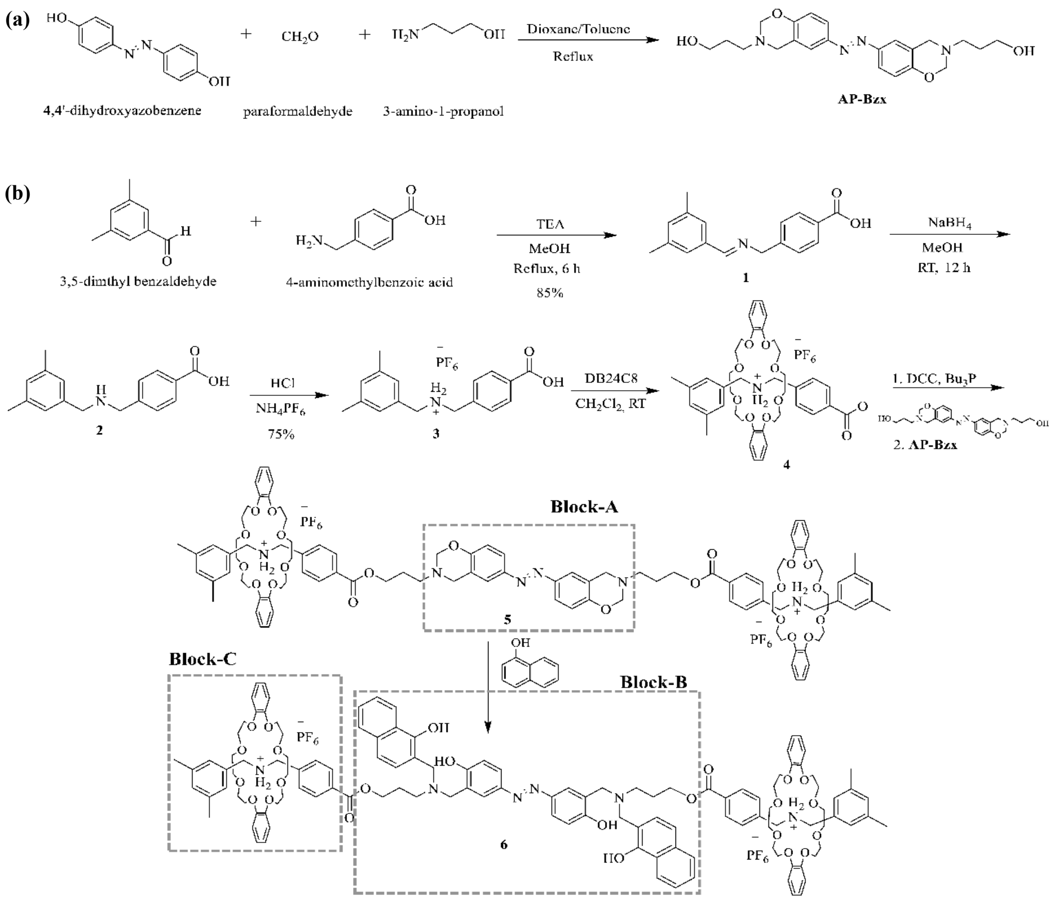
Compound 7 (20 mg, 0.01 mmol) was dissolved in chloroform (2 mL). An excess amount of $CuCl_2$ (15 mg, 0.11 mmol) was added to the solution and left stirring for 2 h. The solution was dried by evaporation to obtain $7/Cu^{2+}$.

3. Results and discussion

3.1 Preparation and characterization of 5

Compound 5 was prepared as shown in Scheme 1. The preparation of AP-Bzx was accomplished by using a light responsive phenol, i.e. azophenol, in combination with aminoalcohol. The Mannich reaction was carried out using 4,4-dihydroxyazobenzene (Scheme 1(a)). The aminoalcohol was used to obtain AP-Bzx. In this way, the benzoxazine obtained contains an -OH group at the terminal for further conjugation with the charge containing molecule (3). The AP-Bzx was characterized by ^1H-NMR (Figure 1(a)).

The terminal end of 5 was designed by using tertiary ammonium ion end capped with a 3,5-dimethylbenzyl group. The reaction between 3,5-dimethylbenzaldehyde and 4-aminomethylbenzoic acid in the presence of triethylamine in methanol resulted in 1. The product was characterized by ^1H-NMR as shown in Figure 1(b). The presence of a methine proton signal at 8.33 ppm and the integral ratios of other signals support the formation of 1 [28]. Compound 1 was reduced by $NaBH_4$ followed by protonation using HCl and anionic exchange using NH_4PF_6. The absence of a methine proton in the ^1H-NMR spectrum indicates the successful reduction of 1 and the formation of 3 (Figure 1(c)). Then, the interlocking of crown ether with the terminal group of 5 by mixing 3 with DB24C8 in dry dichloromethane. It should be noted that the neat 3 was insoluble in dichloromethane; however, when 3 interact with the crown ether, the compound obtained, 4, became soluble. In the next step, AP-Bzx was conjugated with 4 using DCC and Bu_3P. The product obtained was purified by preparative GPC and characterized by ^1H-NMR and MALDI-TOF-MS. The ^1H-NMR signal of crown ether shifts from 4.15 ppm, 3.90 ppm, and 3.80 ppm to 4.64 ppm, 4.41 ppm, and 4.10 ppm indicate the formation of rotaxane (Figure 1(d) and Figure 1(e)). Moreover, MALDI-TOF-MS also supports the molecular weight of 5 at 1,956.20 Da which refers to M-PF_6 (Calc. M-PF_6 = 1957 Da) (Figure 2).



Scheme 1. Synthesis of 6.

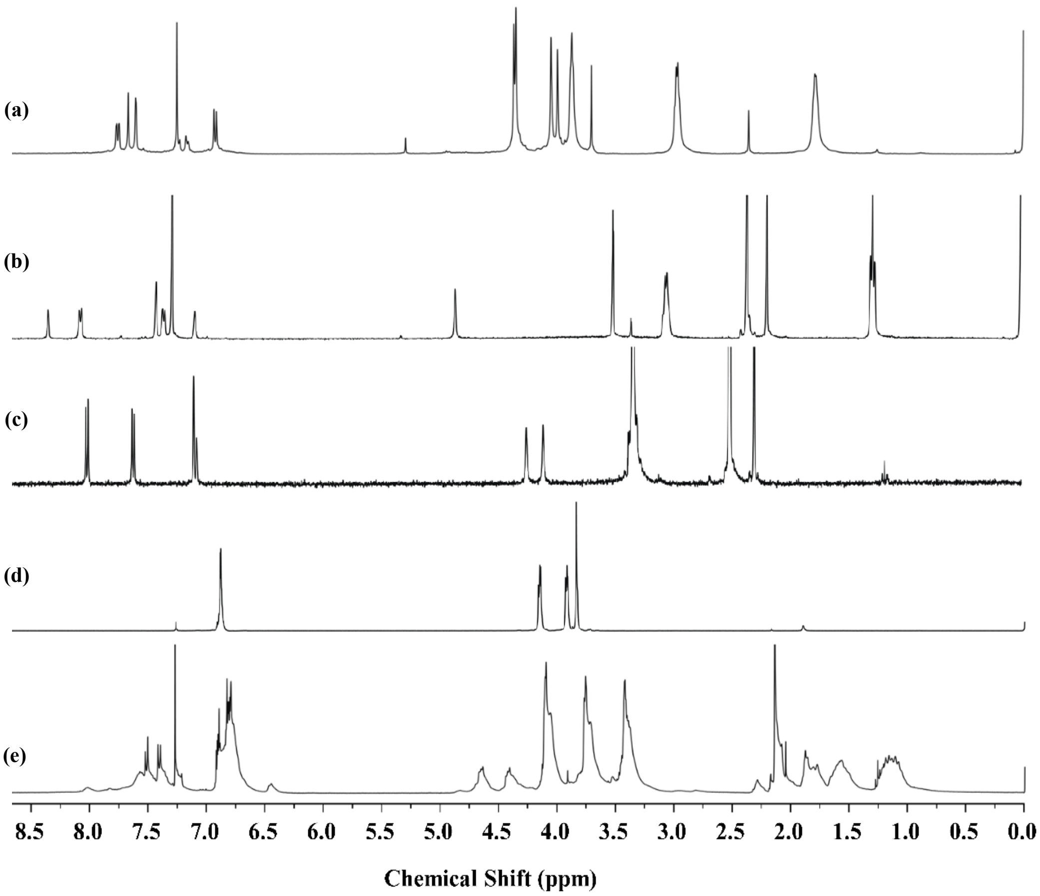


Figure 1. ^{1}H-NMR Spectra of (a) AP-Bzx, (b) 1, (c) 3, (d) DB24C8, and (e) 5.

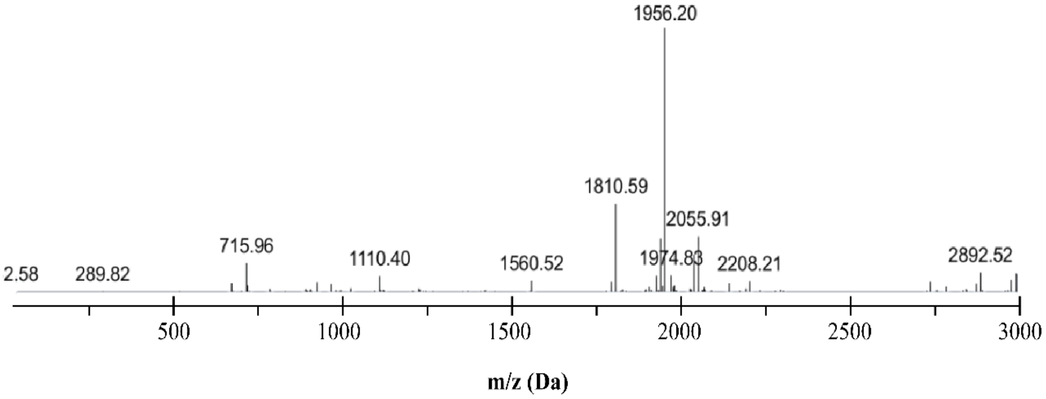


Figure 2. MALDI-TOF-MS Spectrum of 5.

3.2 Ring opening reaction of 5

The ring opening of Block-A in 5 can be achieved by adding phenol to result in Block-B in 6.

3.3 Shuttling of 6 to be 7

The rotaxane shuttling provides dynamic interaction. The methylation was carried out to induce the rotaxane shuttling by mixing 6 with paraformaldehyde, triethylamine and NaBH(OAc)$_3$ in NMP at 70°C. The product was purified by preparative GPC. The shifting proton signal referring to DB24C8 of 6 indicates the successful synthesis of 7. Moreover, the shuttling was investigated by 2D NOESY NMR. The spectrum shows the correlation of the proton signal at 4.0 and 6.75 referring to the -CH$_2$- proton of DB24C8 and the protons on the aromatic ring (Figure 3). This indicates that the methylation of 6 at Block-C moiety leads to the shuttling of DB24C8 to the adjacent aromatic ring.

3.4 Light responsive behavior and fluorescent property

It should be noted that the fluorescent moiety in the Block-B also changes depending on the shuttling of DB24C8. The fluorescent behavior of 6 and 7 were investigated using 10^{-5} M solution in chloroform. It was found that the fluorescent excitation and emission wavelengths of 6 are 480 nm and 565 nm, respectively (Figure 4(a)). In contrast, for 7, they are 320 nm and 455 nm, respectively (Figure 4(b)). The fluorescent behavior of these two molecules is different. This implied the difference in charge transfer mechanism between the naphthalene unit and DB24C8 [29]. For 7, the excitation and emission peaks are relatively higher energy than those of 6. This means the charge transfer is more effective indicating the lowering of distance between two moieties as illustrated in Figure 4(c) and Figure 4(d).

As Block-B contains an azobenzene unit which is a light responsive functional group, the cis/trans conformational change of azobenzene in 7 was studied by exposing 7 solution to UV light. The fluorescent intensity of 7 was traced over UV exposure time. The increase in fluorescent intensity after UV exposure for 1 h without the shift of the fluorescent spectrum suggested that the cis-form of azobenzene greatly restricted the movement of molecule compared to the trans-form, especially the large parts from azo-benzene moiety close to each other. Thus, the rotation in the cis-form would be highly reduced, meaning less energy loss in the internal conversion resulting in an increase in the fluorescent intensity (Figure 5). After exposing the solution to room light for 24 h (VIS light), the fluorescent signal of solution showed almost the same intensity of the 7 solution before UV exposure. This indicated that the cis/trans conformational change of azobenzene moiety is reversible.

3.5 Metal ion complexation

In the past, our group studied benzoxazine dimer and metal ion complexation by X-ray single crystal analysis indicating its metallosupramolecular structure [10,12]. In this work, in order to access the metal ion complexation in 7, $CuCl_2$ was added to a 7 solution in chloroform. Metal ion complexation was traced by fluorescent behavior. The 7/ Cu^{2+} clearly shows different fluorescent emission compared with 7 (Figure 6(a)). It might be due to the formation of copper complexation with benzoxazine dimer affects the energy transfer mechanism as there are 3 different peaks in the fluorescent emission (Figure 6(a) (1)). The effect of UV light on the fluorescent behavior of 7/ Cu^{2+} was also studied. After exposing 7/ Cu^{2+} solution to UV light, the fluorescent emission spectrum is the same but increases in intensity (Figure 6(a) (2)). It is also because of the less molecular movement of the cis conformation as illustrated in (Figure 6(b)). The reversible change of cis/trans conformation of azobenzene moiety investigated fluorescent intensity was also found in 7/ Cu^{2+} solution.

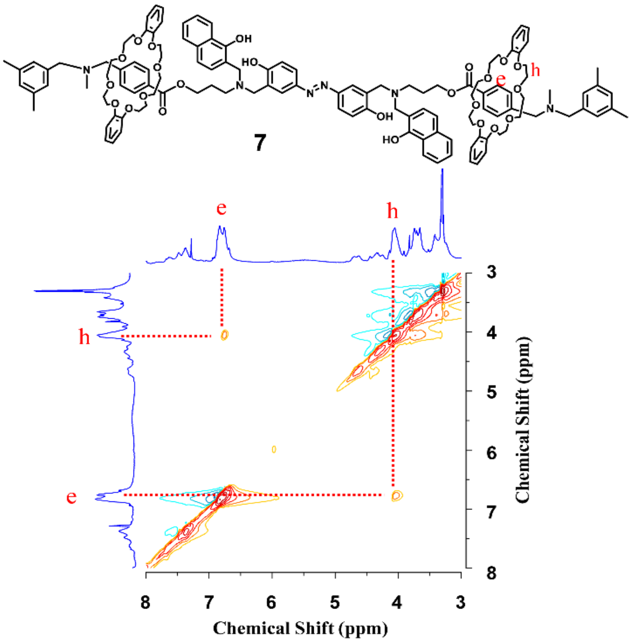


Figure 3. 2D NOESY NMR of 7.

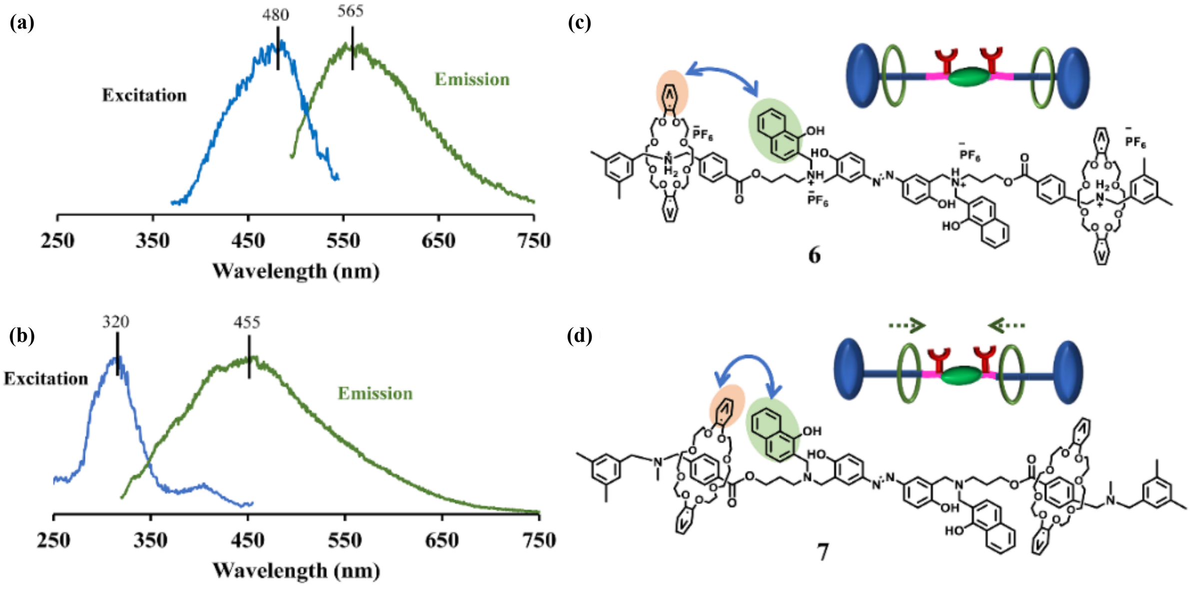


Figure 4. Excitation and emission fluorescent spectra of (a) 6 and (b) 7. Schematic illustrations of (c) 6 and (d) 7.

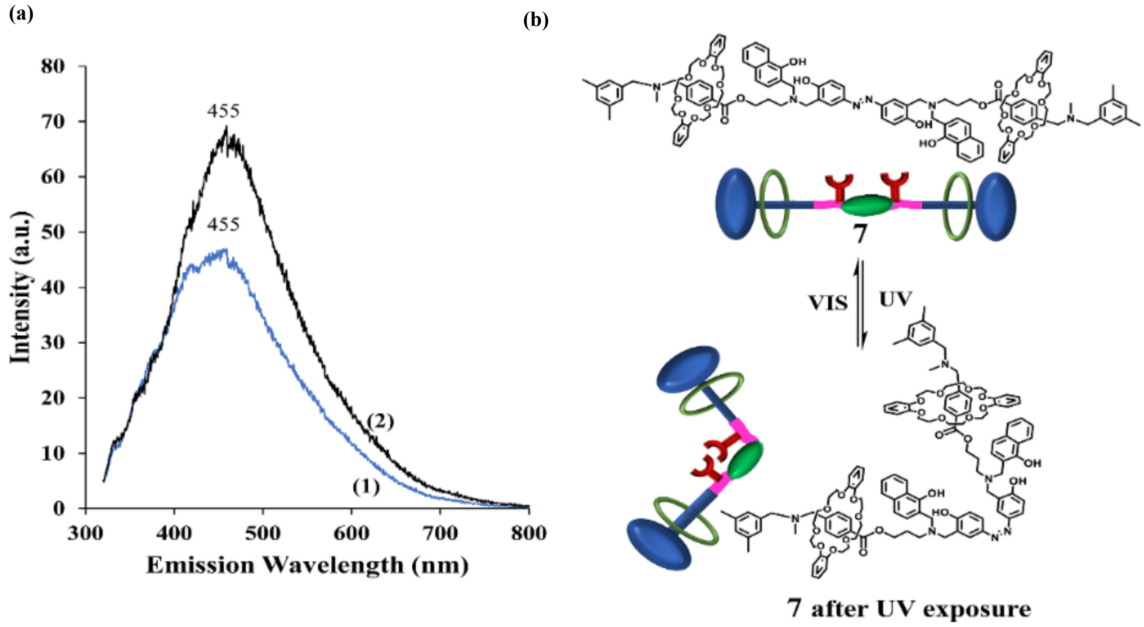


Figure 5. (a) Emission fluorescent spectra of 7 (1) before and (2) after UV exposure and (b) schematic illustration of 7 upon UV/VIS exposure.

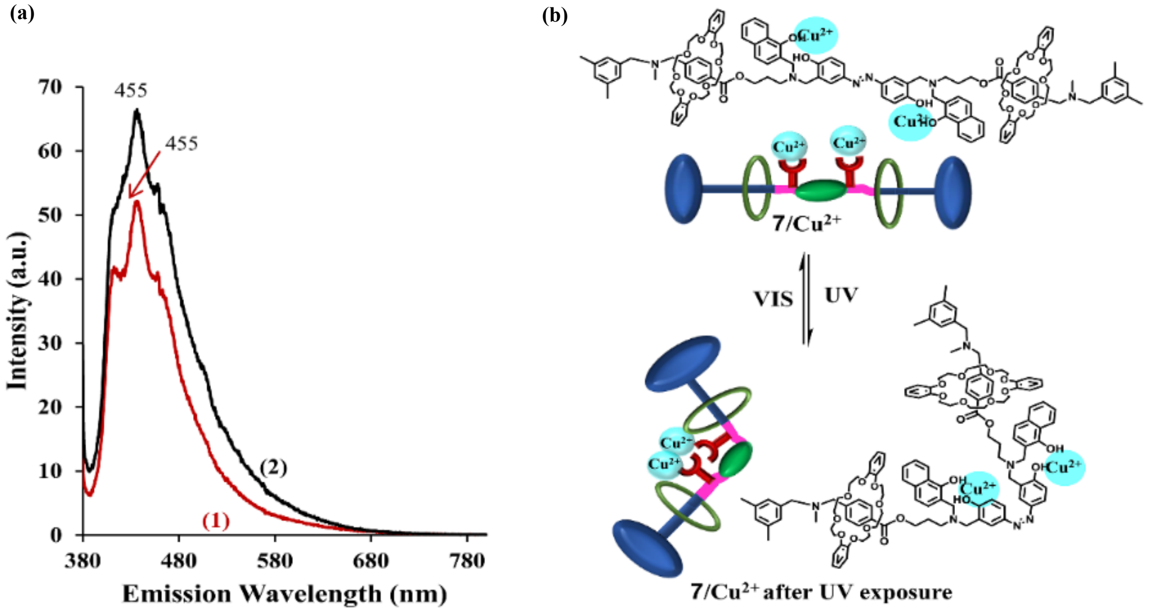


Figure 6. (a) Emission fluorescent spectra of (1) 7/ Cu^{2+} and (2) 7/ Cu^{2+} with UV and (b) Schematic illustration of 7/ Cu^{2+} and 7/ Cu^{2+} with UV exposure.

4. Conclusions

The present work demonstrated a benzoxazine containing rotaxane system with light and metal ion responsiveness. Benzoxazine with multi-responsive functions can be achieved by simply choosing a light responsive phenol and functional amine for further conjugation with the rotaxane system. The ring opening of benzoxazine allows us to access metal ion complexation. In this work, the conjugation of a light responsive benzoxazine with a rotaxane system followed by ring opening reaction using a fluorescent phenol achieves a multi-responsive benzoxazine containing rotaxane system. The product showed light responsive behavior with an increase in fluorescent intensity. Moreover, the copper (II) responsiveness leads to changes in fluorescent emission spectra. The rotaxane shuttling also affects the fluorescent behavior of the molecule. The present work clarifies an approach for multi-responsive rotaxane using a fluorescent labeled benzoxazine dimer. In the future, rotaxane might be able to be used as fluorescent enhancement. This might allow us to increase the sensitivity of light responsive behavior.

Acknowledgements

This research project is supported by Ratchadapiseksompotch Fund Chulalongkorn University.

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