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Title: Selective Recognition of Phenazine by 2,6-Dibutoxynaphthalene-Based Tetralactam Macrocycle

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Selective Recognition of Phenazine by 2,6-Dibutoxynaphthalene-Based Tetralactam Macrocycle

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Summary of main observation and conclusion A 2,6-dibutoxynaphthalene-based tetralactam macrocycle was designed and synthesized. This macrocycle shows highly selective recognition to phenazine -- a well-known secondary metabolite in bacteria and an emerging disinfection byproduct in drinking water. In contrast, the macrocycle shows no binding to the structurally similar dibenzo-1,4-dioxin. It was revealed that hydrogen bonding, π - π and σ - π interactions are the major driving forces between phenazine and the new tetralactam macrocycle. A perfect complementarity in electrostatic potential surfaces may explain the high selectivity. In addition, the macrocycle shows fluorescent response to phenazine, demonstrating its potential in fluorescent detection of phenazine.

Background and Originality Content

Phenazine, an N-heterocyclic polyaromatic hydrocarbon, widely exists in biology and environment. Phenazine and its derivatives are well-known secondary metabolites in many bacteria.^[1] Phenazine is also a common dye and is used in chemical sensing,^[2] optoelectronic materials^[3] and other fields.^[4] Recently, phenazine was identified as a disinfection byproduct in drinking water.^[5] The toxicity of phenazine to human has been investigated and the latest research reveals phenazine to have a minor cytotoxic antiproliferative effect but significant genotoxicity to human.^[6,7] Due to the wide distribution in environment, selective recognition of phenazine is crucial for its sensing and remediation. As shown in Figure 1a, phenazine contains two hydrogen bonding acceptor nitrogen atoms and is structurally planar. A good synthetic receptor should be complementary to the electrostatic potential surface of phenazine in its cavity. Tetralactam macrocycles with four inward-directed amide NHs would be an ideal receptor for phenazine.^[3]

Over the last decades, several tetralactam macrocycles have been reported as synthetic receptors,^[8-12] which were applied in various fields, including chemical sensing,^[13] molecular machines,^[14,15] fluorescent imaging,^[16] organocatalysis^[17] and separations.^[18] They show high affinity to guests containing hydrogen bonding acceptors.^[19] The known tetralactam macrocycles could be divided into three categories according to the type of their sidewalls: angular arene, planar arenes, and aliphatic sidewalls (Figure 1b). When compared to tetralactam macrocycles with angular arene and aliphatic sidewalls, the ones

with planar arene sidewall should be more structurally complementary to planar phenazine. Additional π ··· π or σ ··· π interactions may be involved between the planar sidewalls and phenazine besides hydrogen bonding. The planar aromatic sidewalls of tetralactam macrocycles are currently limited to benzene, anthracene and their derivatives. Phenyl sidewalls are too narrow to interact with phenazine. In addition, anthracene and phenazine are both electron-rich and it may not be favorable for them to have attractive π ··· π interactions.^[20,21] Although the tetralactam macrocycle with anthracene as sidewalls was reported to be able to encapsulate phenazine in solid state, the solution complexation was not studied.^[3] Naphthalene may be a good compromise as sidewalls to maximize σ ··· π interactions with phenazine. However, tetralactam macrocycles with naphthalene as sidewalls were rarely studied.^[22]

During the last six years, we reported a series of naphthol-based macrocyclic receptors which have been used in molecular recognition,^[23,24,25] molecular sensing,^[26-29] molecular machine,^[30] cooperative self-assembly^[31] and supramolecular hydrogel.^[32] We recently synthesized a tetralactam macrocycle with 2,3-dibutoxynaphthalene.^[22] In this article, we report the synthesis and characterization of 2,6-dibutoxynaphthalene-based tetralactam macrocycle (**TM1**) and its selective recognition to phenazine in nonpolar solvent. The macrocycle shows rather high binding selectivity to phenazine and show no binding at all to structurally similar dibenzo-1,4-dioxin.

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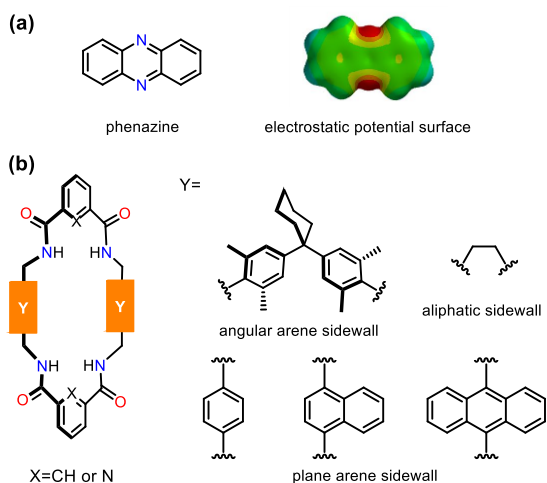
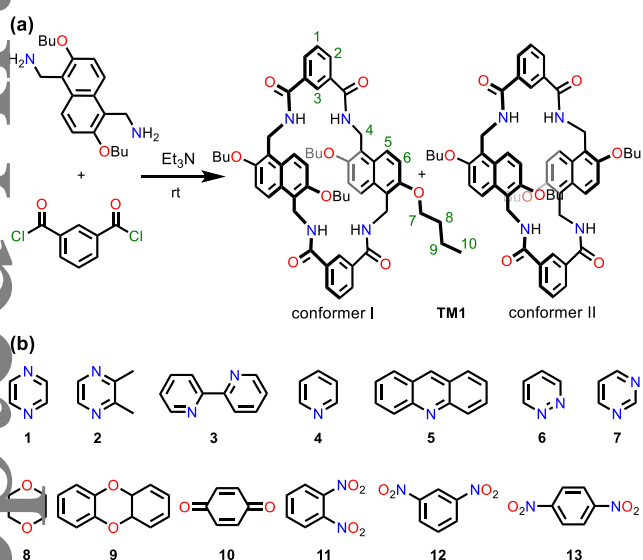


Figure 1 (a) Chemical structure and electrostatic potential surface of phenazine, and (b) representatives of the known tetralactam macrocycles.



Scheme 1 (a) Synthetic route of tetralactam macrocycle **TM1**; (b) chemical structures of neutral guests 1-13.

Results and Discussion

Synthetic route of macrocycle **TM1** is shown in Scheme 1. The diamine and isophthaloyl dichloride react under a pseudo-high dilution condition in the presence of Et_3N at room temperature, affording tetralactam macrocycle **TM1** with a yield of 20%. Electrospray ionization (ESI) mass spectra support the isolated product to be the [2+2] macrocycle **TM1** (see Supporting Information).

There are two conformations for **TM1** because of the flipping of the two 2,6-dibutoxynaphthalenes (Scheme 1). These two conformations should give the same number of peaks with different chemical shifts in the NMR spectrum. If they coexist, two sets of NMR signals should be expected. However, only one set of

signals are observed in the ^1H NMR spectrum of **TM1** (Figure 2a), suggesting that either only one conformation is predominant in the solution or the conformational interconversion is fast at the NMR timescale. When lowering the temperature to 223 K (Figure 2), the NMR peaks were split into two sets, supporting the existence of two different conformers.

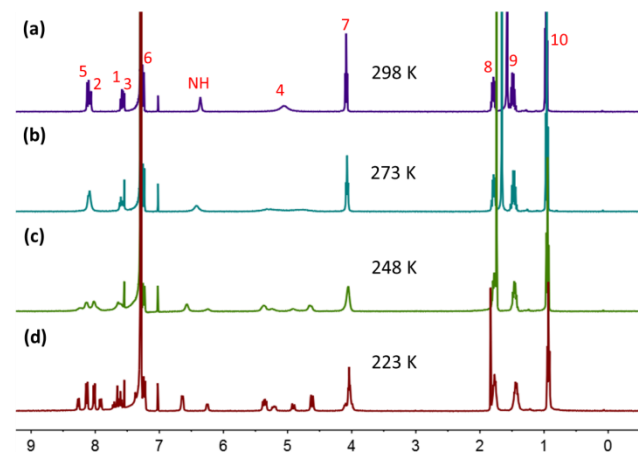


Figure 2 ^1H NMR spectra (400 MHz, CDCl_3) of **TM1** at (a) 298 K, (b) 273 K, (c) 248 K and (d) 223 K.

Single crystal of **TM1**, which is suitable for X-ray crystallography, was obtained by slow evaporation of its solution in acetone. The crystal structure (Figure 3) clearly shows that **TM1** adopts a chair conformation with the two 2,6-dibutoxynaphthalenes in a parallel orientation. The structure contains four water molecules, two of which and two solvent acetone molecules are trapped in the cavity. All the four amide NH residues are directed into the cavity. Isophthalamide NH protons and the phenyl CH protons are hydrogen-bonded to the oxygen atoms of the cavity water molecules (for $\text{N-H}\cdots\text{O}$: $\text{H}\cdots\text{O}$ distance, 2.19 Å; for $\text{C-H}\cdots\text{O}$: $\text{H}\cdots\text{O}$ distance, 2.24 Å); while they are further hydrogen-bonded to the acetone molecules through $\text{O-H}\cdots\text{O}$ ($\text{H}\cdots\text{O}$ distance, 2.06 Å) and $\text{O}\cdots\text{H-C}_{\text{acetone}}$ ($\text{O}\cdots\text{H}$ distance, 2.64 Å) hydrogen bonds. The two other water molecules connect the adjacent **TM1** macrocycles through $\text{H-O-H}\cdots\text{O}=\text{C}$ hydrogen bonds ($\text{H}\cdots\text{O}=\text{C}$ distance, ca. 1.92 Å). In addition, there is a hydrogen bond to the cavity water molecule of yet another adjacent **TM1** macrocycle ($\text{OH}\cdots\text{OH}_2$ distance, 1.86 Å). The two acetone molecules are aligned in a line and threaded through the cavity defined by the two 2,6-dibutoxynaphthalenes. This crystal structure suggests macrocycle **TM1** should be a good host for the guests with complementary shape and hydrogen-bonding acceptors.

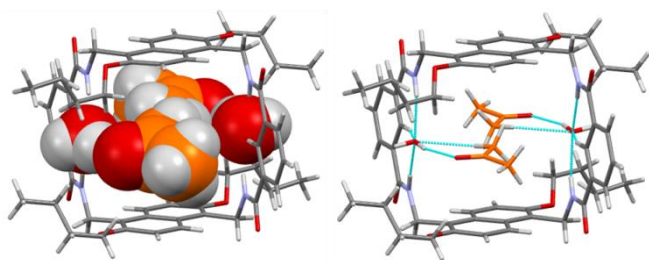


Figure 3 X-ray single crystal structure of **TM1** obtained from its acetone solution.

Macrocycle **TM1** is indeed a receptor for phenazine. In the ^1H NMR spectrum of the equimolar mixture of **TM1** and phenazine, significant upfield shifts were observed for the naphthalene protons of the host and the aromatic protons of the guest when compared to the ^1H NMR spectra of their free states (Figure 4). This suggests that phenazine should be encapsulated in the cavity of **TM1** and the naphthalenes and the phenazine are mutually located in the shielding region of each other. Meanwhile, the amide NH protons shift downfield, suggesting hydrogen bonding between the amide protons and the guest exists. This further supports that phenazine should be encapsulated in the cavity of **TM1**. The broadened signals may be caused by the intermediate exchange rate of the host-guest complex at the NMR timescale. Job's plot supports a 1:1 binding stoichiometry (Figures S1 and S2).

Table 1 Association constants K_a (M^{-1}) of **TM1** to the guests as determined by ^1H NMR titrations.

phenazine	1	2	3	8
780	24	130	68	6.9

Macrocycle **TM1** is highly selective to phenazine among other similar compounds. Thirteen additional guests were selected for comparison. All these guests contain nitrogen or oxygen atoms as hydrogen bonding acceptors. Since binding in the cavity of **TM1** would cause obvious upfield shift of the guest signals, simple ^1H NMR experiments of their 1:1 mixtures were performed to evaluate the binding (Figures S3 - S15). Compounds **1** - **3** and **8** are proven to be guests for **TM1**. No obvious binding was detected for other guests. The binding constants of phenazine, guests **1** - **3** and **8** were determined by ^1H NMR titrations (Figures S16 - S25) and are listed in Table 1. In general, these guests show much weaker binding affinity than phenazine (780 M^{-1}). The binding constant of **TM1** to phenazine was also confirmed by UV-Vis titration (Figures S26 and S27).

Guests **1** - **3** contain two nitrogen atoms which are

positioned in an appropriate distance to satisfy the hydrogen bonding of two isophthalamides. In contrast, guests **4** - **7**, which contain either one nitrogen atom or two nitrogen atoms that are not well positioned for hydrogen bonding with the two isophthalamides of the hosts, are not guests for **TM1**. Consequently, hydrogen bonding is very crucial for the binding of **TM1**. Surprisingly, guests **8** - **13** with oxygen atoms as hydrogen bonding acceptors all show very poor binding to **TM1**. Only guest **8** gives rise to a binding constant of 6.9 M^{-1} ; while the other five guests do not show obvious binding at all. This is in great contrast to the urea/thiourea naphthotubes which can effectively bind these guests.^[23] Most surprisingly, dibenzo-1,4-dioxin **9**, which is structurally very similar to phenazine and contains two oxygen instead of nitrogen atoms, is not a guest to **TM1**. This is even expressed in a control experiment with equimolar mixture of **TM1**, phenazine, and **9** (Figure S28). That is, **TM1** is a very selective receptor to phenazine over other structurally similar compounds.

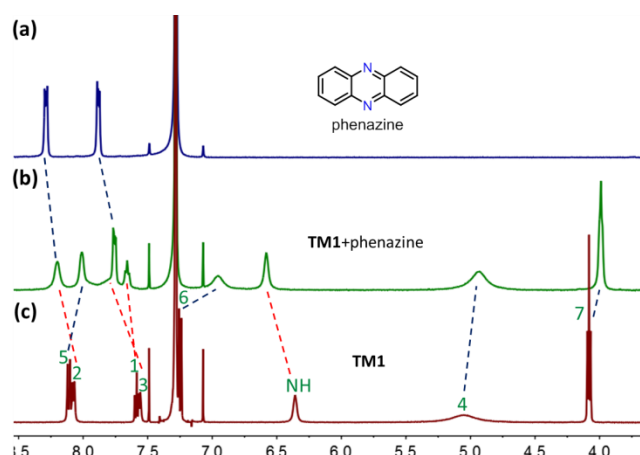


Figure 4 Partial ^1H NMR spectra (500 MHz, CDCl_3 , 298 K, 0.5 mM) of (a) phenazine, (c) **TM1**, and (b) their equimolar mixture.

To understand the high binding selectivity of **TM1** to phenazine, molecular modelling was performed on the complex phenazine@**TM1**. As shown in Figure 5a, four hydrogen bonds ($\text{H}\cdots\text{N}$ distance, 2.40 \AA) between the two nitrogen atoms of phenazine and the four amide protons are formed. Phenazine is sandwiched between the two 2,6-dibutoxynaphthalene sidewalls. Phenazine and the naphthalenes are within the distance (3.65 \AA) of π - π interactions, and σ - π interactions should also be involved. This arrangement is in line with the observation in ^1H NMR spectra. Therefore, $\text{N-H}\cdots\text{N}$ hydrogen bonding, π - π and σ - π interactions should be the major driving force for the binding between **TM1** and phenazine in CDCl_3 .

Theoretically, the binding mode between phenazine and **TM1** should be satisfied by **9** as well. However, no obvious binding was

detected between **9** and **TM1**. Electrostatic potential surface is helpful in explaining this high binding selectivity. As shown in Figure 5b, the electrostatic potential surfaces of **9** and phenazine are rather similar, but the negative charge regions on oxygen atoms of **9** are obviously smaller than those on nitrogen atoms of phenazine. The electrostatic potential surface in the cavity of **TM1** is more complementary to the electrostatic potential surface of phenazine. However, this would not cause binding to **9** at all. We think the additional positive charge on the benzo rings of **9** results in severe repulsion with the amide protons of **TM1**, leading to the complete shutdown of the binding between **TM1** and **9**. This may explain the high selectivity of **TM1** to phenazine over **9**.

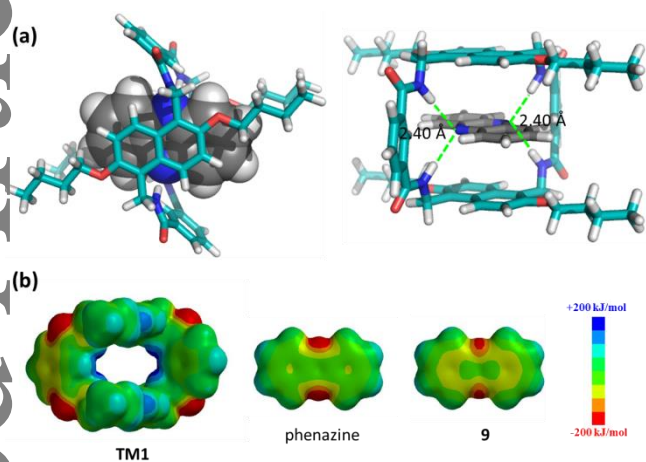


Figure 5 (a) Energy-minimized structure of phenazine@**TM1** at the level of theory of PM6 by using Spartan '14 (Wavefunction, Inc.); (b) Electrostatic potential surfaces of **TM1**, phenazine and **9**.

In addition, tetralactam macrocycle **TM1** is fluorescent because of the 2,6-dibutoxynaphthalene sidewalls. The UV-Vis absorption spectrum was shown in Figure 6a, and the maximal peaks are located at 243, 283 and 350 nm. The optimal excitation wavelength is at 350 nm with an emission peak at 378 nm. The quantum yield of **TM1** is ca. 9.0% in CH_2Cl_2 . The fluorescent response of **TM1** to phenazine was also investigated. As shown in Figure 6b, the addition of phenazine into the solution of **TM1** causes significant quenching of its fluorescence. Therefore, **TM1** may be used as a fluorescent sensor for phenazine in solution.

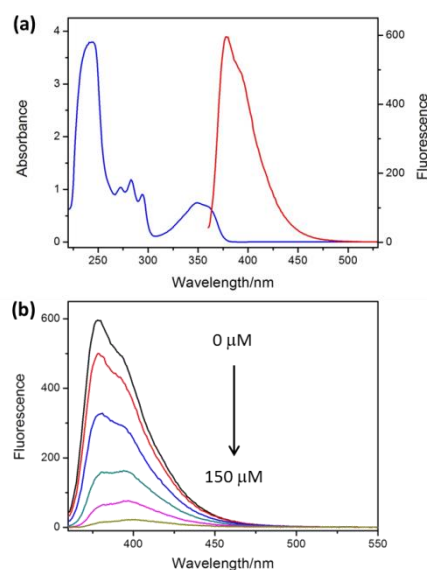


Figure 6 (a) Absorption spectrum (blue line) and fluorescence emission spectrum (red line) of **TM1** in CH_2Cl_2 ; (b) fluorescence emission spectra of **TM1** (10 μM) upon addition of different concentrations of phenazine (0 - 150 μM) in CH_2Cl_2 .

Conclusions

In summary, we reported the synthesis and characterization of a new tetralactam macrocycle based on 2,6-dibutoxynaphthalene. This macrocycle shows rather high binding selectivity to phenazine – a well-known secondary metabolite in bacteria and an emerging disinfection byproduct in drinking water. It was revealed that hydrogen bonding, π - π and σ - π interactions are the major driving forces for the binding, and perfect complementarity in electrostatic potential surfaces of the guest and the host determine the high binding selectivity. Furthermore, efficient fluorescent quenching of the macrocycle upon adding phenazine was observed. Therefore, the 2,6-dibutoxynaphthalene-based tetralactam macrocycle may be used as a fluorescent sensor for phenazine. Although the binding and sensing was achieved in nonpolar solvent rather than water, phenazine may be extracted from water and is then detected in organic solvents. This is quite common for the detection of environmental contaminants in water.³³

Experimental

General method. All the reagents involved in this research were commercially available and used without further purification unless otherwise noted. Solvents were either employed as purchased or dried prior to use by standard laboratory procedures. NMR spectra were recorded on Bruker Avance-400

(500) spectrometers. All chemical shifts are reported in ppm with residual solvents as the internal standards. Electrospray-ionization time-of-flight high-resolution mass spectrometry (ESI-TOF-HRMS) experiments were conducted on an applied biosystems Elite ESI-QqTOF mass spectrometry system. Fluorescence spectra were obtained on a Shimadzu RF-5301pc spectrometer. UV-vis absorption spectra were obtained on a Hitachi U-2600 UV-vis spectrophotometer. Absolute fluorescence quantum yields were recorded with Hamamatsu absolute FL quantum yield spectrometer C11347.

Synthetic Procedure of Macrocyclic TM1: The solution of the 2,6-dibutoxynaphthalene diamine (0.66 g, 2.0 mmol; see Scheme 1) in 60 mL dry CH₂Cl₂ and the solution of isophthaloyl dichloride (0.40 g, 2.0 mmol) in dry CH₂Cl₂ (60 mL) were added slowly through a syringe pump with two syringes to the solution of Hünig's base (3.4 mL, 20.0 mmol) in CH₂Cl₂ (300 mL) over a period of 10 h at room temperature. The resulting mixture was stirred for another 6 h. Solvents were removed under vacuo, and the residue was dissolved in CH₂Cl₂ (50 mL). The organic layer was washed with 10% aqueous HCl (50 mL) followed by saturated aqueous NaHCO₃ (100 mL) and dried over Na₂SO₄. After removing the solvent, the residue was subjected to column chromatography (SiO₂, CH₃OH/CH₂Cl₂ = 1/100) to afford **TM1** (0.18 g, 20%) as a white solid.

Supporting Information

The supporting information for this article is available on the WWW under <https://doi.org/10.1002/cjoc.2018xxxxx>.

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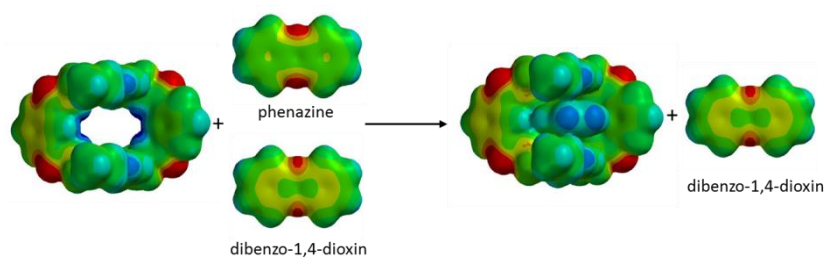
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