



# Host-guest interaction of rotaxane assembly through selective detection of ferric ion: Insight into hemin sensing and switching with sodium ascorbate



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## ABSTRACT

A mechanically interlocked host rotaxane was synthesized by incorporation of tetraphenylethylene and phenanthroimidazole units in the axle to exhibit significant emission bands and demonstrate host-guest interactions via its topologically constrained cavity, and thus to induce a significant and selective fluorescence quenching of rotaxane towards ferric ion ( $\text{Fe}^{3+}$ ). The quenching efficiencies of rotaxane with both ferric ion ( $\text{Fe}^{3+}$ ) and bio-molecular Hemin (containing ferric ion) were investigated to compare the sensitivities of rotaxane for ferric ion and bio-molecular Hemin. The present study could probe host-guest interactions of rotaxane with ferric ion ( $\text{Fe}^{3+}$ ) and Hemin as well as monitoring the biological conversion of Hemin to Heme in presence of sodium ascorbate (as a reducing agent), where the reduced non-toxic Heme could be generated from the toxic form of Hemin.

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## 1. Introduction

Mechanically interlocked architecture molecules with topologically constrained ring structures through non-covalent linkages have attracted much attention from several research groups during last few decades. The excellent molecular recognition of mechanically interlocked systems are significantly offered by various guest and host molecules [1]. Recently, the self-motivated behavior of mechanically interlocked molecules (MIMs) have played a crucial role for vital developments in nanotechnological applications [2], including molecular memory [3], mechanical actuators [4], and drug delivery vehicles [5]. The properties of molecular switches and machines associated with MIMs are pronounced to control the dynamics of MIMs in the presence of external stimuli, which have been well studied and established in recent research [6]. Based on the aforementioned concept, some specific optical (perylene bisimides) [7] or electrochemical (ferrocene) [8,9] receptor groups have been frequently employed. Once incorporated into interlocked molecules, these receptor groups have specific signal transduction

properties and prominent selectivities towards sensing guest species [10–12]. Therefore, the design and construction of MIMs with specific groups [13] can provide an excellent platform towards probing the host-guest interactions for specific molecular recognitions [14–19]. Due to external stimuli, MIMs binding with cations are capable of showing different emission colors or intensity changes [20–26]. In addition, host-guest sensors based on fluorometric changes have received much attention due to their potential applications in environmental science, chemistry, biology, and medicine [27–30]. The challenges of developing unique water-soluble structures have been reported recently based on molecular switches in aqueous solution [31–34], where most biological applications are possible via supramolecular chemistry [35,36].

The photophysical phenomena of luminogenic compounds originated from host-guest complexation and aggregation induced emission (AIE) are non-emissive when soluble in good solvents but become highly emissive as aggregated species in poor, which have been studied and investigated over last decade [37,38]. Many aromatic compounds and dyes have the ability to exhibit AIE including hexaphenylsilole, anthracene, and pyrrole derivatives [39], owing to the restriction of intramolecular motions (RIM). Presently, tetraphenylethylene (TPE) is one of the most favorite units due to its extraordinary AIE behavior [40–43]. Therefore, several reports

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have demonstrated the utilization of AIE in a variety of fields, such as chemical sensors [44], stress sensors [45], explosive detections [46], and biosensors [47]. Importantly, a fluorescent sensor based on the phenanthroimidazole (PIZ) unit with a less intense emission in contrast to the aggregated TPE unit has been reported [48]. Therefore, the combination of TPE and PIZ units were finely tuned for fluorescence emissions towards selective analytes.

Herein, the synthesis of rotaxane **R1** incorporated with TPE and PIZ units as axle components was accomplished via the conventional metal template method [49]. Interestingly, the AIE behavior of the designed **R1** was visualized with bright blue emissions in semi-aqueous solutions of DMSO with high water content. However, the emission band from the PIZ unit of **R1** (i.e., no AIE phenomenon) was observed in pure and semi-aqueous (with low water contents) DMSO solutions. Interestingly, the presence of Fe<sup>3+</sup> ion quenched the fluorescence of both TPE and PIZ chromophoric units in semi-aqueous conditions selectively by means of host-guest interactions into the topologically constrained cavity of **R1**. Moreover, the selectivity of Fe<sup>3+</sup> in the cavity of **R1** was further visualized as fluorescence quenching with ferric ion containing biomolecular Hemin with an enhanced sensitivity, where the quenching efficiency was measured by the extent of AIE from the TPE as well as the fluorescence of PIZ. However, the fluorescence emission of **R1** in a system with a lower water content was proportionally enhanced in the presence of the antioxidant sodium ascorbate and thus to signify the existence of Heme as a result of conversion of Hemin to Heme [50]. Such a conversion could be probed by the generation of optical events in **R1**. This study represents the first example of significant interactions of a macromolecular rotaxane with cyclic ferriprotoporphyrin IX, along with probing the transformation of Hemin (containing ferric ion Fe<sup>3+</sup>) into Heme (containing ferrous ion Fe<sup>2+</sup>) by means of an antioxidant (sodium ascorbate).

## 2. Experimental section

### 2.1. Materials

All reagents and most solvents were purchased from Aldrich Chemicals and used without further purification. Solvents were degassed by freeze/thaw/pump cycle technique, and tetrahydrofuran (THF), chloroform (CHCl<sub>3</sub>), dichloromethane (DCM), acetonitrile (MeCN), and *N,N*-dimethylformamide (DMF) were dried prior to use. All reactions were carried out under nitrogen atmosphere. The following compounds, including 2,7-dibromophenanthrene-9,10-dione [49], 3-(2-bromoethoxy)phenol [49], 2,6 bis(bromomethyl)pyridine [51], 4-(1,2,2-triphenylvinyl)phenol [52], and macrocycle Pd-complex (MCC) [52], were prepared according to the literature procedures.

### 2.2. Characterization

NMR spectra were recorded on Varian Inova 400 and Bruker DRX-300 Avance series (<sup>1</sup>H: 300, 400, MHz; <sup>13</sup>C: 100 and 75 MHz) at 298 K. The chemical shifts were reported in parts per million (ppm) from low to high fields and referenced to residual solvents (<sup>1</sup>H and <sup>13</sup>C, CDCl<sub>3</sub> δ = 7.26 ppm and δ = 77.23 ppm; DMSO-*d*<sub>6</sub> δ = 2.49 ppm and δ = 39.56 ppm, respectively). All values of coupling constant (*J*) were reported in Hertz (Hz). The standard abbreviations of multiplicities were used as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. In addition, UV–Vis spectra in different solvents were obtained by a Jasco UV600 spectrophotometer using 1 cm quartz cuvette. Fluorescence measurements were performed with HITACHI 4000 Series Spectrophotometer. PL emission and excitation spectra were collected

(slit: 5 nm, 10 nm, PMT voltage: 650 V, 450 V, scan limit: 1200 nm/min) for the detector response and the lamp output. Elemental analyses were conducted on HERAEUS CHN-OS RAPID elemental analyzer. High resolution mass spectroscopic (HRMS) measurements were performed using Bruker Daltonics Flex Series ESI mass via a buffer solution of α-cyano-4-hydroxycinnamic acid (CHC). Thin layer chromatographies (chromatographies were performed on Merck silica gel under pressure using TLC) were performed on glass plates coated with silica 60 F24 (Merck). The plates were visualized using ultra-violet light (256 nm) and developed using an iodine chamber.

### 2.3. Synthesis

#### 2.3.1. {5,10-Dibromo-2-(4-(prop-2-yn-1-yloxy)phenyl)-3a,11b-dihydro-1H-phenanthro[9,10-d]imidazole} (1)

A mixture of 2,7-dibromophenanthrene-9,10-dione (2.0 g, 5.50 mmol), 4-(prop-2-yn-1-yloxy) benzaldehyde (2.2 g, 13.77 mmol), and ammonium acetate (6.36 g, 82.63 mmol) in acetic acid (40 mL) was refluxed overnight. After completion of the reaction, the reaction mixture was cooled to room temperature and poured into water (500 mL). The resulting precipitate material was filtered, and washed with water and hexane sequentially. The material was dried overnight under vacuum at room temperature. The crude compound was crystallized from ethanol to give the target compound as a colorless solid material (2.6 g, 93%). mp: > 195 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K) δ (ppm): 13.30 (s, 1H, NH), 8.64–8.56 (m, 4H, ArH), 8.178 (dd, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.18 (dd, *J* = 8.8 Hz, 2H), 4.90 (s, 2H), 3.61 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ (ppm): 158.7, 150.3, 136.9, 128.2, 126.5, 124.4, 123.6, 121.2, 115.6, 79.4, 78.9, 56.0, 40.5, 40.3, 40.1, 39.9, 39.7, 39.4, 39.2.

#### 2.3.2. {5,10-Dibromo-1-hexyl-2-(4-(prop-2-yn-1-yloxy)phenyl)-3a,11b-dihydro-1H phenanthro[9,10-d]imidazole} (2)

To a solution of compound 1 (2.5 g, 4.9 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.04 g, 14.82 mmol) in DMF (10 mL), iodoethane (2.19 mL, 14.82 mmol) was added and heated at 70 °C. After 6 h, the reaction mixture was poured into ice water (100 mL) and extracted with EtOAc (150 mL). The isolated organic layer was washed with brine (250 mL), and then concentrated under vacuum. Then, the crude residue was subjected to column chromatography (silica gel, EtOAc/hexane: 1/4) to give a colorless solid (2.8 g, 95%). mp: > 180 °C. IR (KBr, cm<sup>-1</sup>): 3306, 3085, 2976, 2901 (propargyl), 2855, 2141, 1660, 1555, 1400, 1310, 1251, 1115. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K) δ (ppm): 8.85 (d, *J* = 2.4 Hz, 1H), 8.41 (d, *J* = 6.4 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.18 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 4.78 (s, 2H), 4.42 (t, *J* = 7.6 Hz, 2H), 2.58 (s, 1H), 1.87 (t, *J* = 7.6 Hz, 2H), 1.29–1.24 (m, 6H), 0.84 (t, *J* = 6.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ (ppm): 158.6, 152.9, 137.4, 131.2, 128.6, 125.1, 124.4, 123.2, 1231.2, 115.2, 78.1, 76.7, 75.9, 55.9, 46.7, 31.0, 30.1, 26.0, 22.4, 13.9. HRMS (ESI) (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>27</sub>Br<sub>2</sub>N<sub>2</sub>O, 589.0485, found: 591.0466.

#### 2.3.3. {3-(2-Azidoethoxy)phenol} (3)

To a solution of 3-(2-bromoethoxy)phenol (2.5 g, 11.62 mmol) in DMF (20 mL), the sodium azide (1.51 g, 23.25 mmol) was added and then the reaction mixture was heated at 65 °C overnight. After the completion of reaction, the reaction mixture was poured into ice water (100 mL) and extracted with EtOAc (350 mL). The organic layer was dried over MgSO<sub>4</sub> and then the solvent was evaporated under vacuum. The crude residue was purified by column chromatography (silica gel, EtOAc/hexane: 1/1) to afford a transparent oil (1.8 g, 86%). mp: > 60 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K) δ (ppm): 7.13 (t, *J* = 8.0 Hz, 1H), 6.53–6.43 (m, 3H), 4.02 (t, *J* = 4.8 Hz,

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