Review article

Nonheme iron(II) complexes of macrocyclic ligands in the generation of oxoiron(IV) complexes and the catalytic epoxidation of olefins

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Received 6 December 2005; accepted 13 December 2005
Available online 3 February 2006

Abstract

Mononuclear nonheme oxoiron(IV) complexes bearing 15-membered macrocyclic ligands were generated from the reactions of their corresponding iron(II) complexes and iodosylbenzene (PhIO) in CH 3CN. The oxoiron(IV) species were characterized with various spectroscopic techniques such as UV–vis spectrophotometer, electron paramagnetic resonance, electrospray ionization mass spectrometer, and resonance Raman spectroscopy. The oxoiron(IV) complexes were inactive in olefin epoxidation. In contrast, when iron(II) or oxoiron(IV) complexes were combined with PhIO in the presence of olefins, high yields of epoxide products were obtained. These results indicate that in addition to the oxoiron(IV) species, there must be at least one more active oxidant (e.g., Fe 117-OIPh adduct or oxoiron(V) species) that effects the olefin epoxidation. We have also demonstrated that the ligand environment of iron catalysts is an important factor in controlling the catalytic activity as well as the product selectivity in the epoxidation of olefins by PhIO.

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Keywords: Biomimetic oxidation; Nonheme iron complex; Oxoiron(IV) intermediate; Oxygen activation; Olefin epoxidation

1. Introduction

Enzymes containing mononuclear nonheme iron active sites play key roles in dioxygen activation and the oxidation of hydrocarbons in biological systems [1–4]. The most often-encountered oxidation reactions by the enzymes are alkane hydroxylation, olefin epoxidation, aromatic ring cis-dihydroxylation, and oxidative aromatic ring cleavage [1,4]. A number of mononuclear nonheme iron complexes have been synthesized as chemical models of the nonheme iron enzymes and used as catalysts in a variety of oxygenation reactions including alkane hydroxylation and olefin epoxidation [5–9]. Various artificial oxidants such as hydrogen peroxide (H 2O 2), alkyl hydroperoxides (ROOH), m-chloroperbenzoic acid, and iodosylbenzene (PhIO) have been utilized as oxygen atom donors, and oxygenated products such as alcohols and ketones in alkane hydroxylation and epoxides and cis-diols in olefin epoxidation are produced in high yields [10–13]. It has been proposed that iron-based oxidants, such as iron(III)-peroxo, iron(III)-hydroperoxo, and high-valent iron(IV or V)-oxo species, are responsible for the oxygenation reactions [14–17]. However, the exact nature of the active oxidant(s) and the mechanism of oxygen atom transfer from the intermediates to organic substrates remain elusive and are the topics of current research in the bioinorganic chemistry community.

High-valent iron-oxo species have been frequently invoked as the key reactive intermediates in mononuclear nonheme iron enzymes as well as in heme iron enzymes [18–22]. Very recently, mononuclear nonheme oxoiron(IV) species have been identified in enzymatic and biomimetic
reactions. For example, an intermediate with a high-spin oxoiron(IV) unit was observed in the catalytic cycle of *Escherichia coli* taurine:

\[ \text{KG dioxygenase (TauD)} \] [23–27]. The intermediate was characterized with various spectroscopic techniques such as UV–vis spectrophotometer, electron paramagnetic resonance (EPR), electrospray ionization mass spectrometer (ESI MS), Mössbauer, extended X-ray absorption fine structure (EXAFS), and resonance Raman spectroscopy [23–26]. The decay rate of the intermediate was significantly influenced by the substitution of the C–H bond of taurine with deuterium (e.g., \( 28 < k_H/k_D < 50 \)), implying that the high-spin Fe(IV)-oxo species is a C–H abstracting intermediate [24,27]. In biomimetic studies, mononuclear nonheme oxoiron(IV) complexes bearing tetradentate N4 and pentadentate N5 ligands were synthesized and characterized with various spectroscopic techniques including X-ray crystallography [28–45]. The oxoiron(IV) species have shown reactivities in a variety of oxidation reactions including alkane hydroxylation, olefin epoxidation, alcohol oxidation, and the oxidation of sulfides and PPH3 [28–40]. Thus, elucidation of the chemistry of the long-sought mononuclear nonheme oxoiron(IV) intermediates began by isolation and characterization of the oxoiron(IV) species in enzymatic and biomimetic studies. As our ongoing efforts to understand the chemistry of nonheme iron intermediates, we have prepared two nonheme iron(II) complexes bearing 15-membered macrocyclic ligands, \([\text{Fe}^{II}(\text{TAPH})]^{2+} (1a)\) (TAPH = 1,4,8,12-tetraazacyclododecane) and \([\text{Fe}^{IV}(\text{TAPM})]^{2+} (1b)\) (TAPM = 1,4,8,12-tetramethyl-1,4,8,12-tetraazacyclododecane) (see Chart 1 for the ligand structures), and investigated their chemical properties in the generation of oxoiron(IV) complexes, \([\text{Fe}^{IV}(\text{TAPH})(\text{O})]^{2+} (2a)\) and \([\text{Fe}^{IV}(\text{TAPM})(\text{O})]^{2+} (2b)\), and the catalytic epoxidation of olefins by PhIO.

2. Experimental

2.1. Materials

All chemicals obtained from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated. PhIO was prepared from iodo benzene diacetate by a literature method [46]. The ligand TAPH was obtained from Aldrich Chemical Co. The ligand TAPM was prepared from the methylation of TAPH according to the reported procedures [47,48].

High-spin iron(II) complexes, 1a and 1b, were synthesized by stirring equimolar amounts of \( \text{Fe(OTf)}_2(\text{OTf} = \text{CF}_3\text{SO}_3) \) with TAPH and TAPM, respectively, under inert atmosphere at room temperature. Crystals were obtained by vapor diffusion of diethyl ether into the reaction solutions (ca. 70–80% yield). Elemental analysis calcd. (%) for 1a, \( \text{C}_{17}\text{H}_{32}\text{F}_6\text{FeN}_6\text{O}_6\text{S}_2; \) C, 31.4; H, 5.0; N, 12.9; F, 17.5. Found: C, 31.1; H, 5.2; N, 12.5; F, 17.3%. Elemental analysis calcd. (%) for 1b, \( \text{C}_{17}\text{H}_{34}\text{F}_6\text{FeN}_4\text{O}_6\text{S}_2; \) C, 32.7; H, 5.5; N, 9.0; F, 18.3. Found: C, 32.8; H, 5.8; N, 9.1; F, 18.5%.

2.2. Instrumentation

UV–vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer equipped with OptostatDN variable-temperature liquid-nitrogen cryostat (Oxford Instruments) or with a circulating water bath. Electrospray ionization mass spectra (ESI MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ™ Advantage MAX quadrupole ion trap instrument, by infusing samples directly into the source at 20 μL/min using a syringe pump. The spray voltage was set at 4 kV and the capillary temperature at 70 °C. Elemental Analysis was done on a Thermo Finnigan Italia SpA (Flash EA® 1112) CHN analyzer. 2,5-Bis(5′-tert-butyldimethylsiloxy)benzoazol-2-ylthiophene was used as a reference standard. Resonance Raman spectra were obtained using a liquid nitrogen cooled CCD detector (model LN/CCD-1100-PB, ROPER SCIENTIFIC) attached to a l-m single polychromator (model MC-100DG, Ritsu Oyo Kagaku). An excitation wavelength of 406.7-nm was provided by a Kr⁺ laser (Spectra Physics, BeamLok 2060-RM), with 4 mW power at the sample points. All measurements were carried out with a spinning cell (1000 rpm) at ∼−20 °C. Raman shifts were calibrated with indene, and the accuracy of the peak positions of the Raman bands was ±1 cm⁻¹. Crystallographic analysis was conducted with an SMART APEX CCD equipped with a Mo X-ray tube at the X-ray Crystallographic Laboratory of Ewha Womans University. Product analysis for the epoxidation of cis- and trans-stilbenes was performed on DIONEX Pump Series P580 equipped with a variable wavelength UV-200 detector (HPLC). Products were separated on Waters Symmetry C18 reverse phase column (4.6 × 250 mm), and detection was made at 215 and 254 nm. Product analysis for the epoxidation of other olefins was performed on Agilent Technologies 6890N gas chromatograph (GC) and a Hewlett-Packard 5890 II Plus gas chromatograph interfaced with Hewlett-Packard model 5989B mass spectrometer (GC-MS).

2.3. Crystallographic studies

Crystals suitable for crystallographic analysis were obtained from the layer diffusion of CH₃CN/ether in a glove box. Pertinent crystallographic data and experimental conditions are summarized in Table 1. The structures were solved by using SHELX-86 and SHELX-97 programs.
All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in ideal positions with isotropic displacement parameters. Relevant crystallographic results for 1a and 1b are summarized in Table 1. Complete crystallographic data of 1a and 1b are provided in CIF format (supporting information).

### 2.4. Generation of oxoiron(IV) intermediates

All reactions were followed by monitoring spectral changes of reaction solutions with a UV–vis spectrophotometer. Nonheme oxoiron(IV) complexes, [(TAPM)FeIV =O]2+ (1a) and [(TAPM)FeIV =O]2+ (2b), were prepared by reacting iron(II) complexes (1 mM), Fe(TAPM)(OTf)2 (1a) and Fe(TAPM)(OTf)2 (1b), with 1.2 equiv. PhIO (1.2 mM, diluted in 50 μL of CH3CN) in CH3CN (2 mL) at 20 °C.

### 2.5. Olefin epoxidation by 1 and 2

The reactions of oxoiron(IV) complexes with olefins under stoichiometric conditions were performed by preparing [(TAPM)FeIV =O]2+ (1a) and (TAPM)FeIV =O]2+ (1b) with 1.2 equiv. PhIO (1.2 mM, diluted in 50 μL of CH3CN) in CH3CN (2 mL) at 20 °C. The disappearance of 1a was followed by UV–vis spectral changes of the reaction solution. Product analysis of the resulting solution was performed by GC, GC-MS, and HPLC.

The resulting solution was analyzed with GC, GC-MS, and HPLC. Product yields were determined by comparison against standard curves prepared with known authentic samples. Decane was used as an internal standard for the reactions of cyclohexene, cyclooctene, and 1-octene.

### 3. Results and discussion

The first clean epoxidation of olefins by H2O2 catalyzed by a nonheme iron complex, [FeIII(cyclam)]2+ (cyclam = 1,4,8,11-tetraazacyclotetradecane), was reported by Valentine and co-workers over a decade ago [51]. In the reaction, olefins were converted to the corresponding epoxides with high product yields and stereospecificity. In 2003, the first crystal structure of a nonheme oxoiron(IV) complex bearing a 14-membered macrocyclic ligand, [(TMC)FeIV =O]2+ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), was reported by Münck, Nam, Que, and their co-workers [28]. The [(TMC)FeIV =O]2+ complex was generated from the reaction of [FeII(TMC)]2+ and PhIO in CH3CN at −40 °C, and the characterization of the intermediate was well established by various spectroscopic techniques. Although the oxoiron(IV) species oxygenated PPh3 and sulfides, the intermediate was not capable of activating olefin C=C bond and alkane C–H bond. In the present work, we have prepared nonheme iron(II) complexes bearing 15-membered macrocyclic ligands, [FeII(TAPM)]2+ (1a) and [FeII(TAPM)]2+ (1b), and their corresponding oxoiron(IV) complexes, [(TAPM)FeIV =O]2+ (2a) and [(TAPM)FeIV =O]2+ (2b). In addition, we have investigated the epoxidation of olefins by PhIO in the presence of iron(II) and oxoiron(IV) complexes under stoichiometric and catalytic conditions.

### 3.1. Crystal structures of 1a and 1b

An ORTEP view of the cationic unit of 1a is shown in Fig. 1A. The iron atom is coordinated to four nitrogen atoms of the macrocyclic TAPH ligand with distances of 2.156(4) and 2.159(5) Å, and is slightly out of the plane defined by the four nitrogens of the ligand. The octahedral environment is completed by two CH3CN molecules coordinated in trans positions at 2.199(5) Å. In the structure of 1b (Fig. 1B), the TAPM ligand coordinates the Fe(II) center and the average Fe–N bond distance is 2.245 Å, which is a little longer than the average Fe–N distances of Fe(II) complexes of 14-membered macrocycles, such as [Fe(TMC)(SC6H4-p-OMe)](OTf) and [Fe(thioethyl-Me2cyclam)](PF6) (2.221 and 2.198 Å, respectively) [52]. Different from the structure of iron complexes of 14-membered macrocycles including [Fe(TMC)(O)(CH3CN)]2+ [28], two adjacent N-methyl groups of 1b point above the Fe-ligand plane and the other two below the plane. The OTf anions bound to iron ion direct away from the two N-methyl groups in the same side to avoid a steric hindrance.

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**Table 1**

<table>
<thead>
<tr>
<th>Crystallographic data of <a href="OTf">Fe(TAPH)(CH3CN)2</a>2 (1a) and [Fe(TAPM)(OTf)2] (1b)</th>
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<td><strong>1a</strong></td>
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3.2. Generation and characterization of oxoiron(IV) complexes, 2a and 2b

The reactions of 1a and 1b with PhIO in CH₃CN at −40 °C produced pale green species, 2a and 2b, respectively. While the intermediate 2a showed a high stability even at room temperature \((t_{1/2} \approx 1 \text{ h at } 20 °C)\), the intermediate 2b disappeared within 1 min at −40 °C (Supporting Information, Fig. S1). The UV–vis spectra of the intermediates exhibit broad visible absorption bands at \(\lambda_{max} = 750 \text{ nm for } 2a\) \((\varepsilon = 500 \text{ M}^{-1} \text{ cm}^{-1})\) (Fig. 2A for 2a) and \(\lambda_{max} = 890 \text{ nm for } 2b\) (Supporting Information, Fig. S1); the characteristic near-infrared (IR) absorption bands with a low extinction coefficient indicate the generation of nonheme oxoiron(IV) species \([28–30,38,43]\). Further spectroscopic characterization of the green species was performed with 2a since this intermediate showed a high thermal stability. The EPR spectrum of 2a appeared silent, as observed in other nonheme oxoiron(IV) species \([28–30,41]\). The ESI mass spectrum of 2a exhibited a prominent ion peak at \(m/z = 435\), which upshifts accordingly upon introduction of \(^{18}\text{O}\) when PhI\(^{18}\text{O}\) was used instead of PhI\(^{16}\text{O}\) to generate the intermediate (Fig. 2B). These data are consistent with the formulation of 2a as \([\text{Fe}^\text{IV}-(\text{TAPH})(\text{O})(\text{CF}_3\text{SO}_3)]^+\) (calculated \(m/z\) of 435). The resonance Raman spectrum of 2a with 406.7-nm laser
excitation exhibited a peak at $841\text{ cm}^{-1}$ that shifts to $806\text{ cm}^{-1}$ upon introduction of $^{18}\text{O}$ (Fig. 2C). The observed downshift of $35\text{ cm}^{-1}$ is close to the $34\text{ cm}^{-1}$ value calculated from Hooke’s law for an Fe$=\text{O}$ vibration. Very recently, we have reported the Fe$=\text{O}$ vibrations of oxoiron(IV) complexes of 14-membered TMC ligand bearing different axial ligands [39]. Based on the UV–vis, EPR, ESI MS, and resonance Raman spectral data, 2a was unambiguously assigned as a nonheme oxoiron(IV) complex, $[\text{Fe}^{IV}(\text{TAPH})(\text{O})]^{2+}$.

### 3.3. Nonheme oxoiron(IV) species in olefin epoxidation and catalytic epoxidation of olefins by PhIO

We have shown previously that $[(\text{TPA})\text{Fe}^{IV}=\text{O}]^{2+}$ (TPA = tris(2-pyridylmethyl)amine) reacts with cyclooctene at $-40\,\text{C}$, yielding cyclooctene oxide product [29]. We therefore tested the reactivity of 2a in olefin epoxidation. Upon addition of 50 equiv. of cyclooctene or cyclohexene to the solution of 2a at $20\,\text{C}$, the intermediate decayed back to the starting iron(II) complex with a rate similar to the natural decay of 2a (Supporting Information, Fig. S2). Product analysis of the resulting solution with GC revealed that no oxygenated products were formed in this reaction (Reaction A in Eq. (1)). Also, the reaction of 2b with olefins did not produce oxygenated products either. These results indicate that oxoiron(IV) complexes of 15-membered macrocycles, 2a and 2b, are not capable of oxygenating olefins.

**Equation (1)**

\[
\text{CH}_3\text{CN, 20 °C} \quad \frac{\text{no reaction}}{[(\text{TPA})\text{Fe}^{IV}=\text{O}]^{2+}(2a)} \quad \text{CH}_3\text{CN, 20 °C} \quad \frac{\text{Reaction A}}{\text{Reaction B} + \text{PhIO}}
\]

Interestingly, when PhIO was added to a reaction solution containing 2a and cyclooctene at $20\,\text{C}$, we have observed the formation of both cyclooctene oxide product ($\approx85\%$ based on PhIO added) (Reaction B in Eq. (1)). We therefore carried out the epoxidation of olefins by PhIO in the presence of iron(II) complexes, 1a and 1b, in CH$_3$CN at $20\,\text{C}$. As the results are listed in Table 2, high yields of oxygenated products were obtained in the catalytic epoxidation reactions, but the product yields were different depending on the iron(II) catalysts. In the epoxidation of cyclooctene, cyclooctene oxide was produced as a sole product (Table 2, entry 1). In cyclohexene epoxidation, cyclohexene oxide was produced as a major product with trace amounts of allylic oxidation products such as cyclohexenol and cyclohexenone (Table 2, entry 2). Interestingly, when the cyclohexene epoxidation was carried out in the presence molecular oxygen, allylic oxidation products were yielded predominantly in the reaction of 1b, whereas the product distribution was not changed significantly in the case of 1a (e.g., the yields of cyclohexene oxide, cyclohexenol, and cyclohexenone were 19%, 33%, and 50%, respectively). In the epoxidation of cis- and

### Table 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Products</th>
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<tr>
<td></td>
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<td>Yields (%) of products</td>
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<tr>
<td>1</td>
<td>Cyclooctene</td>
<td>Cyclooctene oxide</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexene</td>
<td>Cyclohexene oxide</td>
</tr>
<tr>
<td></td>
<td>Cyclohexenol</td>
<td>&lt;2</td>
</tr>
<tr>
<td></td>
<td>Cyclohexene</td>
<td>&lt;2</td>
</tr>
<tr>
<td>3</td>
<td>cis-Stilbene</td>
<td>cis-Stilbene oxide</td>
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<tr>
<td></td>
<td>trans-Stilbene oxide</td>
<td>&lt;2</td>
</tr>
<tr>
<td></td>
<td>Benzaldehyde</td>
<td>&lt;2</td>
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<tr>
<td>4</td>
<td>trans-Stilbene</td>
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<tr>
<td></td>
<td>Benzaldehyde</td>
<td>&lt;3</td>
</tr>
<tr>
<td>5</td>
<td>1-Octene</td>
<td>1,2-Epoxyoctane</td>
</tr>
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</table>

| a | Reactions were run at least triplicate under Ar, and the data reported represent the average of these reactions.
| b | The formation of oxygenated products was not observed in the absence of the iron catalysts.
| c | Yields were determined based on the amounts of PhIO added, by comparing with standard curves of known authentic samples.

trans-stilbenes by 1a and PhIO, cis- and trans-stilbene oxides were yielded as major products, respectively, and only small amounts of isomerized epoxide products and benzaldehyde were yielded (Table 2, entries 3 and 4), demonstrating that the olefin epoxidation is highly stereospecific. On the other hand, the epoxidation of cis-stilbene by 1b and PhIO afforded a relatively high yield of trans-stilbene oxide (Table 2, entry 3). Similar to the cyclohexene epoxidation, the presence of O$_2$ in the reaction solution of 1b increased the yields of trans-stilbene oxide and benzaldehyde markedly (e.g., the yields of cis-stilbene oxide, trans-stilbene oxide, and benzaldehyde were 27%, 22%, and 22%, respectively), whereas the formation of trans-stilbene oxide and benzaldehyde was not affected by the presence of O$_2$ in the case of 1a. The different catalytic activity of 1a and 1b was also observed in the epoxidation of 1-octene (Table 2, entry 5), in which only a trace amount of 1,2-epoxide was formed in the reaction of 1b, whereas 1a afforded a moderate amount of the epoxide product. The results presented above demonstrate that the ligand structure of nonheme iron catalysts affects not only the catalytic activity [51] but also the product distributions [53–55] in olefin epoxidation reactions.

### 3.4. Plausible reactive intermediates for olefin epoxidation

We have shown above that high yields of oxygenated products were obtained in the epoxidation of olefins by nonheme iron(II) complexes and PhIO but their corresponding nonheme oxoiron(IV) complexes do not react with olefins. In addition, we have found that the addition of PhIO to a solution containing an oxoiron(IV) complex and cyclooctene afforded a high yield of cyclooctene oxide. These results demonstrate that 2 is not the reactive
intermediate responsible for the olefin epoxidation but there is at least one more active oxidant that effects the olefin epoxidation. In line with the present results, we have reported very recently that nonheme oxoiron(IV) complexes are not able to hydroxylate aromatic rings but when the oxoiron(IV) are combined with perbenzoic acids, the hydroxylation of aromatic rings occurs [56]. Chart 2 depicts plausible oxidants that may be involved in the olefin epoxidation. In line with the present results, we have reported very recently that nonheme oxoiron(IV) complexes are not able to hydroxylate aromatic rings but when the oxoiron(IV) are combined with perbenzoic acids, the hydroxylation of aromatic rings occurs [56]. Chart 2 depicts plausible oxidants that may be involved in the olefin epoxidation by PhIO in the presence of 1 and 2. Those are an Fe IV-OIPh adduct (3) and an oxoiron(V) species (4). The intermediate 3 has been frequently suggested as an active oxidant in metal complex-catalyzed oxidation reactions by PhIO [57–66]. However, no direct evidence for the involvement of the metal-OIPh adduct in oxygen atom transfer has been reported yet. The intermediate 4 has also been frequently proposed in nonheme iron complex-catalyzed oxygenation of hydrocarbons [10–12,17], but such an oxoiron(V) intermediate has not been identified either. Therefore, continued extensive research is needed to identify active oxidant(s) that are involved in the catalytic oxygenation of hydrocarbons by nonheme iron complexes.

4. Conclusion

We have reported the generation and characterization of nonheme oxoiron(IV) complexes with 15-membered macrocyclic ligands. The oxoiron(IV) species were inactive in olefin epoxidation. In contrast, we have obtained high yields of epoxide products in the catalytic epoxidation of olefins by iron(II) complexes and PhIO. In addition, when oxoiron(IV) complexes were combined with PhIO in the presence of olefins, we have observed the formation of epoxide products. These results indicate that there must be another active oxidant whose oxidizing power is stronger than that of the oxoiron(IV) species. We have proposed an Fe IV-OIPh adduct and an oxoiron(V) species as plausible reactive species, although none of these have been identified yet. We have also demonstrated that the ligand environment of iron catalysts is an important factor in controlling the catalytic activity as well as the product selectivity in the epoxidation of olefins by nonheme iron complexes and terminal oxidants.

5. Abbreviations

cyclam 1,4,8,11-tetraazacyclotetradecane
EPR electron paramagnetic resonance
ESI MS electrospray ionization mass spectrometer
PhIO iodosylbenzene

TAPM 1,4,8,12-tetraazacyclotetradecane
TAPH 1,4,8,12-tetraazacyclotetradecane
TauD Escherichia coli taurine:zKG dioxygenase
thioethyl-Me 1-thioethyl-1-1,4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane
TMC 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
TPA tris(2-pyridylmethyl)amine

Acknowledgement

This work was supported by the Ministry of Science and Technology of Korea through Creative Research Initiative Program (to W.N.), the SRC/ERC program of MOST/KOSEF (R11-2005-008-00000-0 to J.K., Y.S.K., and K.M.K.), and the Korea Research Foundation (KRF-2005-217-C00006 to M.S.S.).

Appendix A. Supplementary data


References


Appendix A. Supplementary data


References
