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A supramolecular bifunctional artificial enzyme with superoxide dismutase and glutathione peroxidase activities

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ABSTRACT

For constructing a bifunctional antioxidative enzyme with both superoxide dismutase (SOD) and glutathione peroxidase (GPx) activities, a supramolecular artificial enzyme was successfully constructed by the self-assembly of the Mn(III)meso-tetra[1-(1-adamantyl methyl ketone)-4-pyridyl] porphyrin (MnTPyP-M-Ad) and cyclodextrin-based telluronic acid (2-CD-TeO_3H) through host–guest interaction in aqueous solution. The self-assembly of the adamantyl moieties of Mn(III) porphyrin and the β-CD cavities of 2-CD-TeO_3H was demonstrated by the NMR spectra. In this supramolecular enzyme model, the Mn(III) porphyrin center acted as an efficient active site of SOD and tellurol moiety endowed GPx activity. The SOD-like activity (IC_{50}) of the new catalyst was found to be 0.116 μM and equals to 2.56% of the activity of the native SOD. Besides this, supramolecular enzyme model also showed a high GPx activity, and a remarkable rate enhancement of 27-fold compared to the well-known GPx mimic ebselen was observed. More importantly, the supramolecular artificial enzyme showed good thermal stability.

1. Introduction

It has been established that a variety of human diseases have been generated by oxidative stress of reactive oxygen species (ROS), such as superoxide anion, H_2O_2, organic peroxide, and hydroxyl radical. ROS were generated as byproducts of cellular metabolism and were mainly controlled by antioxidative defense system, especially by antioxidant enzymes [1,2]. In biological organism, the antioxidant enzymes, superoxide dismutase (SOD), catalase (CAT), and glutathione peroxidase (GPx) contribute dominatingly to enhance cellular antioxidative defense against oxidative stress [3–7]. SOD is a metalloenzyme that catalyzes the dismutation of superoxide radical anion ($O_2^{\cdot-}$) to H_2O_2 and O_2. And GPx, a selenium-containing enzyme, functions to catalyze the reduction of H_2O_2 and other harmful hydroperoxides by glutathione (GSH) (Scheme 1) [8,9]. Studies indicated that each enzyme has a specific as well as an irreplaceable function and they act in a cooperative or synergistic way to ensure a global cell protection. It seems that there is a balance between both the activities and the intracellular levels of these antioxidants that are essential for the survival of organisms and their health. This balance was proved to be more important for protection against oxidative stress than the level of any single antioxidant enzyme [10].

Although native antioxidant enzymes are extremely efficient for defensing against oxidative stress, effective therapies utilizing native antioxidant enzymes may be problematic due to concerns with protein instability, short circulation half-lives, high production costs, and potential antigenicity [11], leading to the development of various antioxidant mimetics.

In recent years, there were considerable interests in preparing the enzyme mimics with the properties of SOD or GPx for elucidating catalytic mechanism and for potential pharmaceutical application [12,13]. In order to further study the cooperation of these enzymes in antioxidation and to generate efficient therapeutic agents, bifunctional enzymes with both SOD and GPx activities have been constructed by chemical methods in our group and others. For example, a bifunctional enzyme with SOD and CAT activities was prepared by cross-linking of SOD and CAT [14]. The bifunctional enzymes with both SOD and GPx activities have been designed by using chemical synthesis and mutation of native SOD [15,16]. However, successful construction of a bifunctional enzyme which has both SOD and GPx activities by using a supramolecular method remains a challenge.

Porphyrins are 'the pigments of life' [17]. Due to their high stability and chemical versatility, manganese porphyrins are a promising group of compounds for developing as SOD mimics [18]. Since the earliest report of SOD activity by a manganese porphyrin complex by Pasternack and co-workers with the tetrakis (4-N-methylpyridyl)porphine complex of Mn(III) [19], the Mn(III) (porphyrinato) complexes have been studied by several groups as SOD mimics

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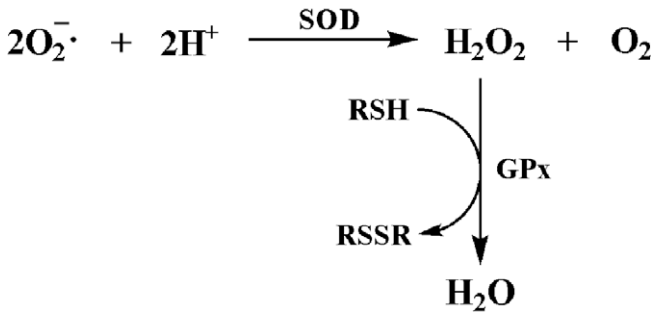


Scheme 1. Catalytic reactions of cooperative action of SOD and GPx.

and were reported to be 0.2–12% of the native SOD activity. The Mn(III) (porphyrinato) complexes have clearly been shown to possess true catalytic and biologic function of SOD mimic by many researchers [12].

β-Cyclodextrin is a cyclic compound consisting of seven glucose units, it is water-soluble and nontoxic. Therefore, it can be used in the human body, such as drug delivery systems [20]. On the other hand, it is known to form inclusion complexes with various low-molecular-weight compounds, ranging from nonpolar aliphatic molecules to polar amines and acids [21]. Thus, it has been used to construct various supramolecular architectures through host–guest interaction [22,23]. For β-cyclodextrin and adamantane derivatives, a typical host–guest pair have induced a lot of interesting development of supramolecular systems for their high association constant [24–26]. Herein, utilizing a 'supramolecular linker' which constructed through the host–guest interaction between adamantane and β-cyclodextrin, a bifunctional artificial enzyme with a porphyrin core and four cyclodextrin-based suspensory tellurol moieties has been designed and prepared. The Mn(III) porphyrin acted as an efficient active site of SOD, and tellurol moiety endowed GPx activity. The catalytic behaviors and the kinetics of the bifunctional enzyme model with both SOD and GPx activities were investigated in detail.

2. Experimental

2.1. Materials

Dimethylbenzene, ethanol, chloroform were purchased from Beijing Chemical Plant. Pyrrole was acquired from Fluka (AR grade). 4-pyridinecarboxaldehyde was purchased from J&K Chemical LTD and used without further purification. 1-adamantyl bromomethyl ketone, xanthine oxidase (XOD) and xanthine were purchased from Aldrich Chemical Co. Ammonium hexafluorophosphate (NH_4PF_6) was obtained from Alfa. Tetrabutylammonium chloride (TBAC) was purchased from Tianjinguangfu Chemical Plant and was used without further purification. β-cyclodextrin (β-CD) was purchased from Tianjin Chemical Plant, and recrystallized three times from distilled water and dried for 12 h at 120 °C in vacuo. DMF was dried by distilling from CaH_2 under the reduced pressure. Column chromatography was performed on silica gel (200–300 mesh) or Sephadex G-25.

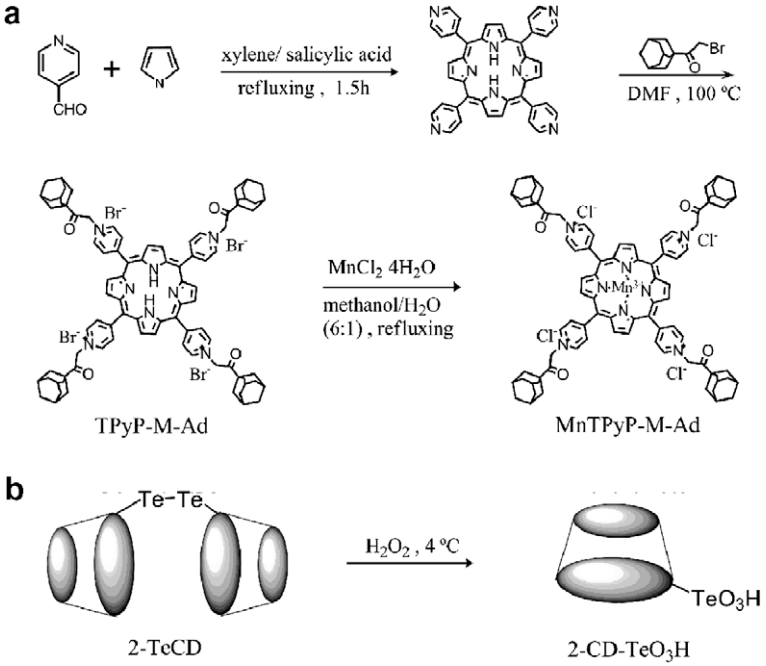
2.2. Instruments and measurements

^{1}H NMR was measured on a Bruker AM-500 spectrometer. The spectrometric measurements were carried out with a Shimadzu 3100 UV–Vis-NIR Recording Spectrophotometer interfaced with a personal computer. Data were acquired and analyzed by using ultraviolet spectroscopy software. The temperature for UV time course studies was controlled within (±) 0.5 °C by use of a LAUDA compact low-temperature thermostat RC6 CP. The buffer pH values were determined with a METTLER TOLEDO 320 pH Meter. Molecular weights of the compounds were measured on an APPLIED BIOSYSTEMS Q TRAP.

2.3. Synthesis

2.3.1. Synthesis of MnTPyP-M-Ad (Scheme 2a)

Meso-tetra(4-pyridyl)porphine (TPyP) was prepared by the literature methods [27–29]. Synthesis of meso-tetra[1-(1-adamantyl methyl ketone)-4-pyridyl] porphyrin (TPyP-M-Ad) followed the known procedures as described in the literature with some alter-



Scheme 2. Synthetic route for MnTPyP-M-Ad (a) and 2-CD-TeO_3H (b).

ation [25,30]. The pyridyl groups in TPyP (203 mg, 0.328 mmol) were quarternized with 1-adamantyl bromomethyl ketone (408 mg, 1.586 mmol) in DMF (40 mL) for 20 h at 100 °C to synthesize TPyP-M-Ad under a nitrogen atmosphere. After being cooled to room temperature, the brown precipitate was collected by filtration and washed with diethyl ether to yield crude product. The crude product was purified by recrystallization from methanol and chloroform (1:2) to yield 300 mg of desired product as a brown solid. ^{1}H NMR (500 MHz, DMSO-d6, 25 °C) δ = –3.03 (s, 2H, –NH), 1.80–1.86 (s, 24H, adamantane), 2.12 (s, 24H, adamantane), 2.18 (s, 12H, adamantane), 6.40 (s, 8H, –$COCH_2$–), 9.142–9.155 (d, J = 5.0 Hz, 8H), 9.182 (d, J = 5.0 Hz, 8H) 9.42 (s, 8H). MALDI-MS: 1327.7 found: 1327.3 (Fig. S1).

Metallation of TPyP-M-Ad: Metallation of TPyP-M-Ad proceeded following standard procedures [31]. Briefly, TPyP-M-Ad (100 mg) and $MnCl_2{\cdot}4H_2O$ (200 mg, ~20 × eq.) were dissolved in methanol/H_2O (6:1, 35 mL) with 1 M NaOH (200 μL) and mixed under refluxing conditions to form MnTPyP-M-Ad. The degree of metallation was assessed by monitoring the soret band shift from 426.5 nm to 463 nm (Fig. 1), with complete metallation observed after approx. 30 min. The MnTPyP-M-Ad was then purified, with the addition of NH_4PF_6 to precipitate the metalloporphyrin, followed by washing with H_2O. Counterion exchange to Cl^- was then achieved by dissolving the product in acetone and metalloporphyrin precipitation upon the addition of TBAC. The final Cl^- form of MnTPyP-M-Ad was then desiccated to dryness 12 h. MALDI-MS: 1379.7 found: 1377.3.

2.3.2. Synthesis of 2-CD-TeO_3H (Scheme 2b) [32]

Dicyclodextrinyl ditelluride (2-TeCD) was prepared as described previously [33,34]. 2-TeCD (100 mg) was dissolved in 15 mL of deionized water with a large excess amount of H_2O_2 (30%, 150 μL) and mixed under stirring condition. The solution was stirred at temperatures between 4 °C over night. The mixture solution was freeze-dried, and then the residue was purified on a column of Sephadex G-25 with distilled water as an eluent. The resulting solution was freeze-dried, and a pure sample was obtained in 72% yield as a white powder. ^{1}H NMR (500 MHz, D_2O): δ = 3.31–4.26 (m, 42H), 4.71–5.14 (m, 7H). MALDI-MS: 1295.6 found: 1296.3.

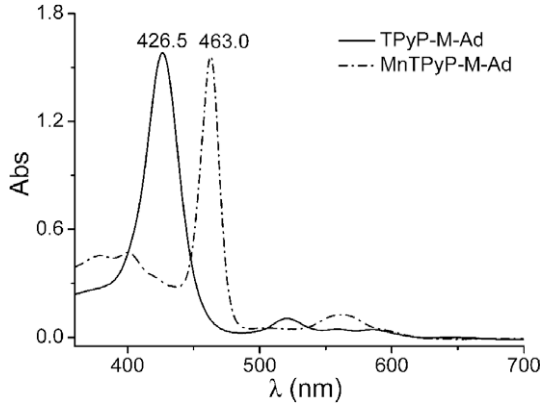


Fig. 1. Absorbance spectra for porphyrin compounds between 380 and 700 nm. The concomitant soret band shift was observed from 426.5 nm (TPyP-M-Ad) to 463 nm (MnTPyP-M-Ad) upon porphyrin metallation.

2.3.3. Preparation of the enzyme model [35]

An aqueous solution of MnTPyP-M-Ad (0.2 mmol, 5 mL) was added dropwise to an aqueous solution of 2-CD-TeO_3H (0.8 mmol, 5 mL), followed by mild ultrasonication for 2 h, giving the inclusion complex (the enzyme model). Model compounds were prepared from TPyP-M-Ad (0.2 mmol, 5 mL) and 2-CD-TeO_3H (0.8 mmol, 5 mL), according to a similar procedure as described earlier (Scheme 3).

2.3.4. Determination of SOD activity

Superoxide radical anions generated by the xanthine/xanthine oxidase system at pH 7.8 (phosphate buffer, 25 °C) were detected by following spectrophotometrically the reduction of nitro blue tetrazelium (NBT) to blue formazane (MF^+) [8,36,37]. The appropriate amount of xanthine oxidase (final concentration of 0.025 U ml^{-1}) was added to an aqueous solution of 100 μM NBT, 300 μM xanthine, 0.1 mM EDTA, and 50 mM phosphate buffer (final volume of 1 mL) to cause a variation of absorbance (ΔA_{560}/min) of 0.013. The reaction rate in blank samples and in the presence of model catalyst was measured for 300 s only, in order to avoid problems coming from the natural inactivation of the enzymatic system.

2.3.5. Determination of GPx activity

The catalytic activity was assayed according to a modified method reported by Hilvert et al. [38–41]. The reaction was carried out at 25 °C in 1.0 mL of phosphate buffer (pH 7.0, 50 mM) containing 0.25 μM compounds catalyst and 115 μM ArSH and 250 μM cumene hydroperoxide (CUOOH). The initial rates for the reduction of CUOOH by were determined by monitoring the disappearance of ArSH at 410 nm (ε_{410} = 14,500 M^{-1} cm^{-1}, pH 7.0) with a Shimadzu 3100 UV–Vis-NIR spectrophotometer. Appropriate control of the nonenzymatic reaction was performed and subtracted from the catalyzed reaction.

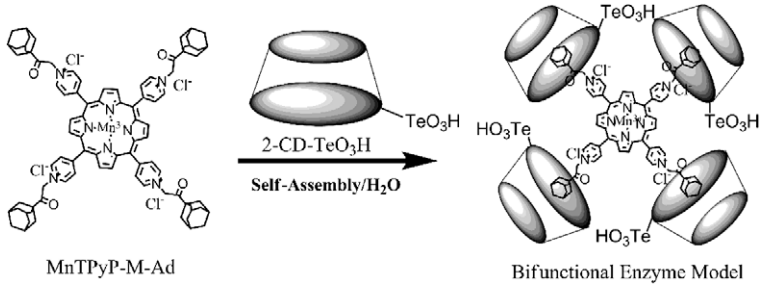
Determination of GPx activity by using 4-nitrobenzenethiol (ArSH) as a substrate (Eq. 1).

$$\mathrm{CUOOH} + 2\mathrm{ArSH} \xrightarrow{\text{catylst}} \mathrm{CUOH} + \mathrm{ArSSAr} + \mathrm{H_2O} \quad (1)$$

3. Results and discussion

3.1. Design and preparation of the artificial enzyme

β-Cyclodextrin, a type of cyclodextrin with seven glucose units, can recognize adamantal moiety well (association constant:



Scheme 3. Schematic representation of the preparation of the enzyme model.

10^{3-4} M^{-1}), and this typical host–guest pair has been widely utilized to build up supramolecular materials and devices [22,24]. Through the host–guest interaction between adamantane and β-CD, a bifunctional antioxidant enzyme mimic was constructed by self-assembly of the MnTPyP-M-Ad and 2-CD-TeO_3H in water (Scheme 3). In order to confirm the host–guest complexation of 2-CD-TeO_3H and the adamantane-containing porphyrin (MnTPyP-M-Ad), model compounds were prepared, and NMR measurements were carried in D_2O at different temperatures. As shown in Fig. S2, the ratio between CD's C_1–H and methylene protons (c) of adamantly group was 7:6, indicating the formation of a 1:4 complex. Furthermore, the signals of methine and methylene protons (a, b, c) of the adamantly group in the supramolecular model shift downfield with an increase in the concentration of 2-CD-TeO_3H at 25 °C, 50 °C and 60 °C, respectively (Fig. 2). It revealed that the inclusion complexation between adamantal moiety and cyclodextrin indeed occurred, and the supramolecular complex showed very good thermal stability [25].

3.2. Catalytic behavior of the artificial enzyme

3.2.1. SOD activity

The SOD activity of the enzyme model was quantified using the standard xanthine/xanthine oxidase assay system first developed by McCord and Fridovich [8,36]. Superoxide anion generation by the xanthine/xanthine oxidase system was detected by following spectrophotometrically the reduction of nitro blue tetrazelium (NBT) to blue formazane (MF^+) at 560 nm. In order to determine the concentration of the catalyst which achieves 50% inhibition (IC_{50}) of the reaction (a generally used indicator for comparing the efficiencies of enzymes and enzyme mimics), the percentage of inhibition against model catalyst concentration was plotted in Fig. 3, and the concentration of catalyst (IC_{50}) which inhibits the rate of the reduction of NBT by 50% (IC_{50}) was found to be 0.116 μM, it equals to 2.56% of the activity of native SOD enzyme (Table 1). However, the SOD activity (IC_{50}) of the guest molecule MnTPyP-M-Ad was only found to be 0.132 μM, and it was lower than the SOD-like activity of the enzyme model. Neither the metal-free ligand nor 2-CD-TeO_3H exhibited any SOD-like activity in subsequent experiments under the same conditions.

3.2.2. GPx activity

3.2.2.1. Catalytic activity. To probe the mechanism of tellurium in catalysis, some of the intermediates possibly involved in the catalytic cycle were characterized. When 2-CD-TeO_3H was added to ArSH in PBS (pH 7.0), the ArSH quickly disappeared by monitoring the UV absorbance at 410 nm, and intermediate telluro-sulfide appeared (Fig. 4) [42]. From this observation, it showed that the Te(VI) of the 2-CD-TeO_3H could be deoxidized into Te(IV), then joined to the catalytic cycle [32].

The GPx activity of catalyst was studied according to a modified method reported by Hilvert et al. [38–41], using 4-nitrobenzenethiol (ArSH) as a thiol substrate. The relative activities of the mimics are summarized in Table 1. For the peroxidase activity, the enzymatic rates were corrected for the background (nonenzymic) reaction between hydroperoxide and thiol. The initial rate of the background (nonenzymic) reaction between CUOOH and ArSH was very slow; the compounds catalyst (1 μM catalytic center) exhibits a remarkable rate enhancement (v_0 = 7.1 μM min^{-1}). For further evaluating the catalytic capacity of the model catalyst, a well-known GPx mimic, ebselen was used for comparation. Under identical conditions, a slight enhancement of the reaction rate was observed when ebselen (1.0 μM) was added (v_0 = 0.26 μM min^{-1}). Assuming that the rate had a first-order dependence on the concentration of catalyst catalyzing the reduction of CUOOH by ArSH (Table 1), the model catalyst was at least 27 times more efficient than ebselen. Compared with 2-CD-TeO_3H catalyst (v_0 = 9.6 μM min^{-1}), the catalytic activity of the model catalyst shows a little lower than it (Fig. 5). Considering that 2-CD-TeO_3H had specific binding cavity for recognizing substrate (ArSH), it is surprising that the model catalyst in which the cyclodextrin cavities were taken up by adamantal moieties displayed high catalytic activity [32]. Compared with other reported GPx mimics, such as telluromicelle [43], the catalytic activity of the compounds catalyst is only a little lower than it. According to the former research [42], electrostatic interaction may possibly play a great contribution to the high catalytic behavior.

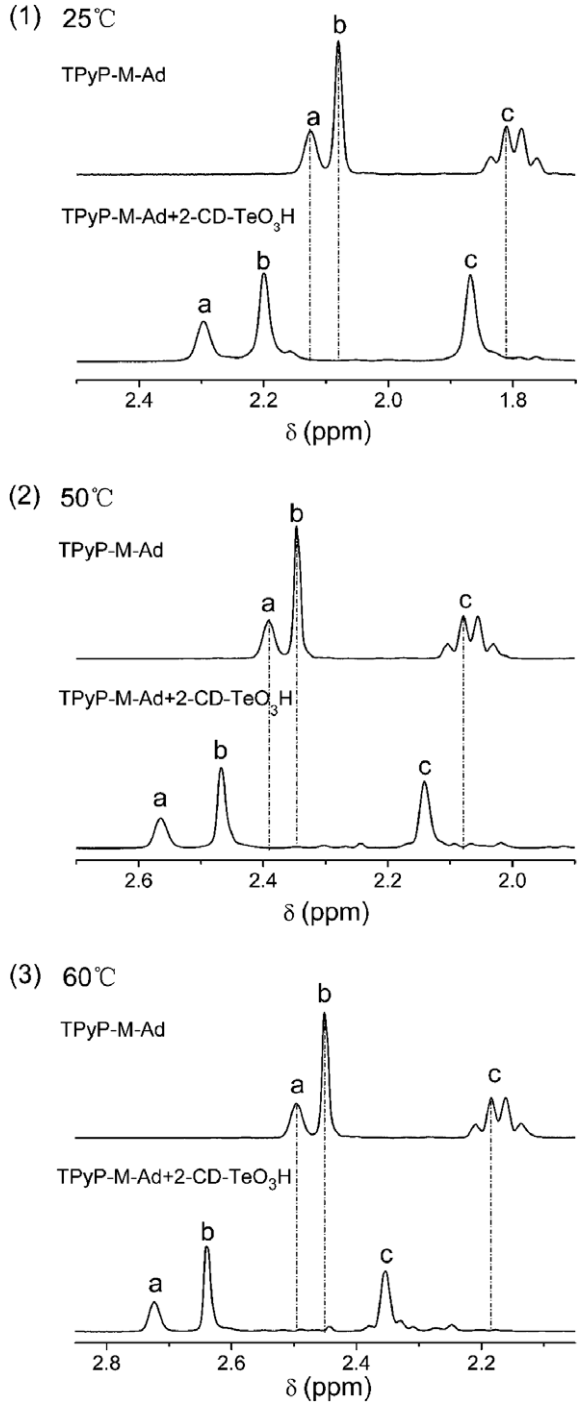


Fig. 2. ^1H NMR spectra of TPyP-M-Ad in 0.059 mM and the complex in 0.059 mM in D_2O at 25 °C, 50 °C, and 60 °C respectively.

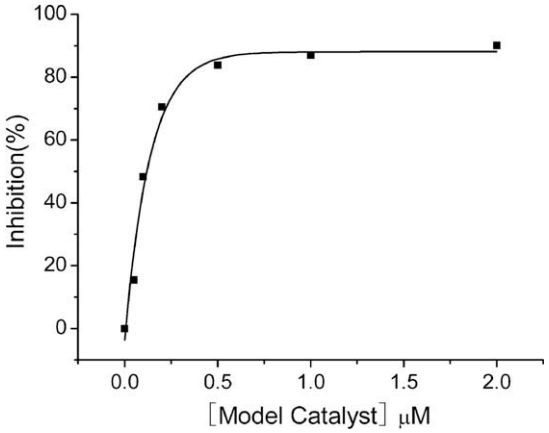


Fig. 3. Percentage of inhibition of NBT reduction by superoxide anion radical versus different concentrations of compounds catalyst.

Table 1
SOD[a] and GPx[b] activities of the catalyst.

Catalysts	GPx activity v_0 (μM min^{-1})	SOD activity	
		IC_{50} (μM)	Relactive activity (%)
Ebselen	0.26	ND	–
Mn(III)-TPyP-M-Ad	ND	0.132	2.25
2-CD-TeO_3H	9.6	ND	–
Model catalyst	7.1	0.116	2.56
Cu, Zn-SOD[c]	–	1.3×10^{-3}	100

[a] SOD activity was carried out in the assaying solution (1 ml), containing 50 mM phosphate buffer (pH 7.8), 0.025 U xanthine oxidase, 100 μM NBT, 300 μM xanthine, 0.1 mM EDTA, and an appropriate amount of catalyst at 25 °C.
[b] GPx activity was assessed in phosphate buffer (50 mM, pH 7.0) at 25 °C with ArSH (115 μM) and CUOOH (0.185 mM), and was corrected for the spontaneous oxidation in the absence of catalyst.
[c] Refs. [8,9,44].

3.2.2.2. Kinetics. To probe the mechanism of the model catalyst promoting the peroxidase reaction, detailed kinetic studies were undertaken. In the presence of the model catalyst (2.0 μM catalytic center) at pH 7.0 (50 mM PBS) and 25 °C, the apparent kinetic parameters of the catalyst were obtained, $v_{(max)} = 77.76$ μM min^{-1}, $k_{cat}^{(app)} = 38.88$ min^{-1}, $Km_{CUOOH} = 3.56$ mM, $k_{cat}^{(app)}/Km_{CUOOH} = 1.09 \times 10^4$ M^{-1} min^{-1} (the initial concentration of ArSH fixed to 100 μM). Typical saturation kinetics was observed in the NBT assay system for the peroxidase-like reaction (Fig. 6). Additionally, a straight line was obtained via double-reciprocal plots (Lineweaver–Burk plots) of initial rate versus substrate concentration (Fig. 7), indicating that this model is a real GPx mimic.

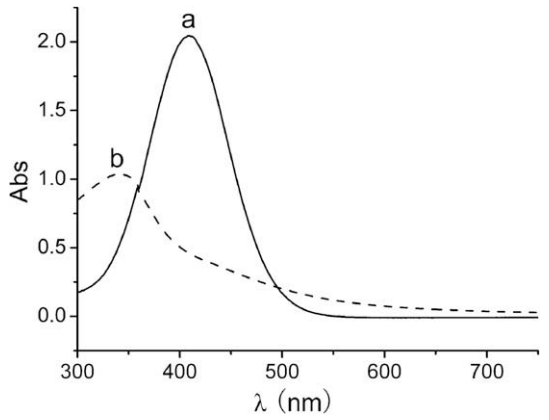


Fig. 4. UV spectra of ArSH (140 μM) in water (curve a), and after adding 2-CD-TeO_3H (curve b).

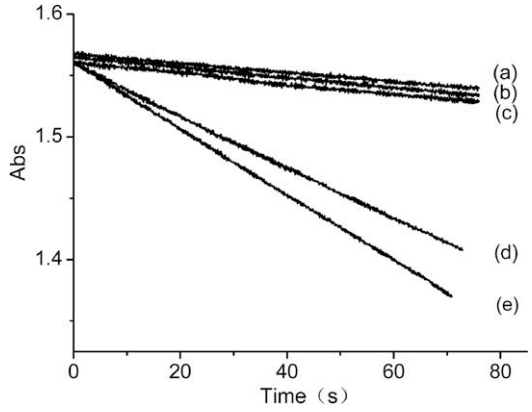


Fig. 5. Plots of absorbance versus time during the catalytic reduction of CUOOH (185 μM) by ArSH (115 μM) at pH 7.0 and 25 °C: (a) no catalyst, (b) 1 μM MnTPyP-M-Ad, (c) 1 μM ebselen, and (d) 0.25 μM model catalyst, (e) 1 μM 2-CD-TeO_3H.

4. Conclusion

In this study, we have successfully designed and prepared an artificial enzyme through host–guest interaction between the adamantyl moieties of Mn(III) porphyrin and the β-CD cavities of 2-

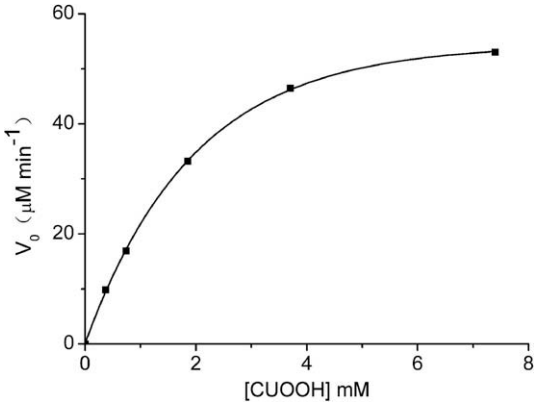


Fig. 6. Plots of initial rates (v_0) at different concentrations of CUOOH in the presence of a compounds catalyst (2.0 μM catalytic center) in PBS (pH 7.0) and 25 °C. The initial concentration of ArSH was fixed to 100 μM. The concentration of CUOOH was 0.37, 0.74, 1.85, 3.7 and 7.4 mM^{-1}, respectively.

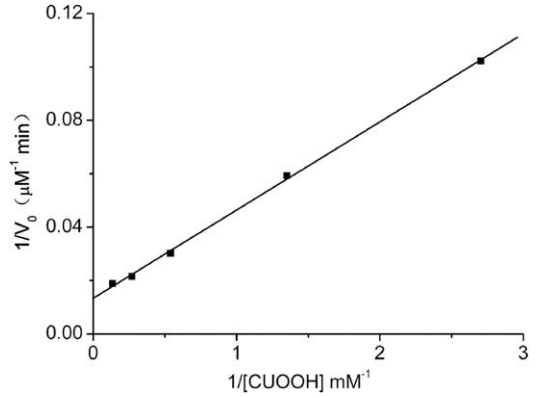


Fig. 7. Lineweaver–Burk plots of the artificial enzyme-catalyzed the reduction of CUOOH by ArSH (2.0 μM catalytic center). The initial ArSH concentration was fixed to 100 μM. The concentration of CUOOH was 0.37, 0.74, 1.85, 3.7 and 7.4 mM, respectively.

CD-TeO_3H in aqueous solution. This new supramolecular enzyme model shows bifunctional antioxidative enzyme activities in which the Mn(III) porphyrin acted as an efficient active site of SOD and tellurol moiety–endowed GPx activity. Compared with other bifunctional antioxidative enzyme mimics, this supramolecular artificial enzyme has its obvious advantage: simple preparation process and remarkable catalytic activity. We anticipate that the supramolecular strategy will provide us a new way for the design of artificial enzymes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bioorg.2010.03.001.

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