

## **Supporting Information** (b918750b)

### **Materials and Methods**

#### **Preparation of ZAIS NCs**

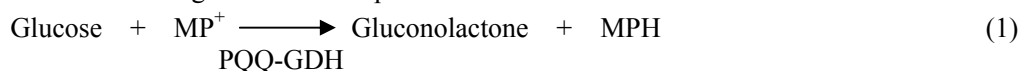
As a precursor, a metal ion-diethyldithiocarbamate complex of  $(\text{AgIn})_x\text{Zn}_{2(1-x)}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_4$  was prepared by mixing metal nitrate and sodium diethyldithiocarbamate aqueous solution with  $0.4 < x < 1.0$ . Two hundred fifty mg of the complex was thermally decomposed at  $180^\circ\text{C}$  for 15 min in  $\text{N}_2$  atmosphere, followed by the addition of oleylamine (OA, 15 mL). Then, it was heated again at  $180^\circ\text{C}$  for 10 min with vigorous stirring. The resulting suspension was centrifuged to remove large particles. ZAIS NCs were separated from supernatant by the addition of methanol. The wet precipitate was washed with methanol several times and dissolved in 7.5 mL of chloroform. The quantum yield of the resulting NCs was 47 % ( $y = 0.8$ ), which was much larger than the value (ca. 24%) that we previously reported [ref. 12 of this manuscript]. This favorable improvement resulted from some modification of the synthesis method and the details will be reported in near future.

#### **Ligand exchange of ZAIS NCs**

Oleylamine-capped ZAIS (OA-ZAIS) NCs were subjected to ligand exchange. Three mL of ethanol solution containing 0.2 M 3-mercaptopropionic acid (MPA) and 0.3 M KOH was added dropwisely to the same amount of OA-ZAIS chloroform solution. The turbid solution was stirred for 3h, followed by centrifugation. The wet precipitate of MPA-capped ZAIS (MPA-ZAIS) NCs were washed with ethanol, and re-dissolved in 3 mL of water. No dissolution or collapse of ZAIS NCs was confirmed by TEM observation although TEM images were not shown in this paper. The quantum yield of the resulting NCs was 46 % ( $y = 0.8$ ), indicating that the above-mentioned procedures for ligand exchange did not influence optical property of ZAIS NCs at all. The water-soluble ZAIS NCs are quite stable even in water; significant decrease in the quantum yield was not detected at least for 1 month.

## Quantitative characteristics of the ZAIS NCs chemosensor

As shown in Figure 3 (c), addition of glucose induces enzymatic reduction of  $MP^+$  to MPH, resulting in increment of the PL intensity. Its magnitude increases with an increase in concentration of glucose added ( $[Glucose]_{add}$ ). The quantitative characteristic of this sensing was considered. The Stern-Volmer equation indicates that  $I_0/I-1$ , where  $I_0$  and  $I$  are the PL intensities in the absence and presence of quenchers, is proportional to the quencher concentration. In the case of our glucose sensing by the PL intensity, the concentration of  $MP^+$  quencher should be determined by  $[Glucose]_{add}$  because the following reaction takes place.



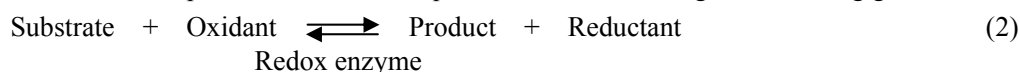
If the reaction stoichiometrically completes every glucose addition, concentration of  $MP^+$  ( $[MP^+]$ ) is determined by the following equation

$$[MP^+] = [MP^+]_o - [Glucose]_{add}$$

where  $[MP^+]_o$  is the initial  $MP^+$  concentration. It is, therefore, expected that plots of  $I_0/I-1$  as a function of  $[Glucose]_{add}$  give a linear relationship and that the PL intensity becomes  $I_0$  at  $[Glucose]_{add} = [MP^+]_o$ , the latter of which is 5  $\mu\text{M}$  in the present case. However, Figure S1 (a) was obtained contrary to our expectation.

In such the case, it would be better to assume that the reaction of eq. (1) is equilibrated reaction. In the case of reactions catalyzed by redox enzymes, it is known that the reaction is held in equilibrium when redox potential of oxidant or reductant is close to that of active center of the enzyme. Since difference in redox potentials between  $MP^+/MPH$  and PQQ-GDH is ca. 60 mV, the above assumption seems to be appropriate.

Here, it is attempted to describe the equilibrium reaction using the following general reaction.



Its reaction constant ( $K$ ) is given by

$$K = [\text{Product}][\text{Reductant}] / [\text{Substrate}][\text{Oxidant}] \quad (3)$$

When the substrate ( $[Substrate]_{add}$ ) is added to the solution containing oxidant of the initial concentration ( $[Oxidant]_o$ ), the following relationships are given.

$$[Oxidant] + [Reductant] = [Oxidant]_o \quad (4)$$

$$[Product] = [Reductant] \quad (5)$$

$$[Substrate] + [Product] = [Substrate]_{add} \quad (6)$$

The relationship between  $[Oxidant]$  and  $[Substrate]_{add}$  is obtained from eqs. (3)–(6) and two calculation lines were shown in Figure S1 (b). Actually, the substrate concentration was given as a ratio of  $[Substrate]_{add} / [Oxidant]_o$  as the normalized value.

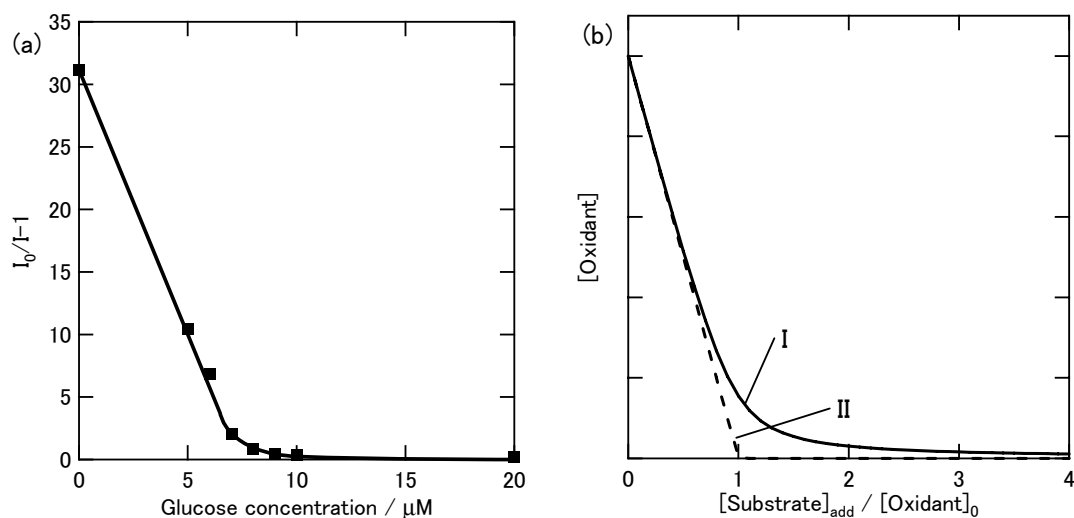


Figure S1. (a) Plots of  $I_0/I-1$  as a function of glucose concentration to the sensing solution containing MPA-ZAIS,  $\text{MP}^+$  ( $5\mu\text{M}$ ), PQQ-GDH (5unit/mL) and PBS (20 mM, pH = 7.0), and (b) numerical simulation of enzymatic reaction in equilibrium states plotted for moderate (I) and infinite (II) equilibrium constant ( $K$ ).

The line II was obtained when  $K$  is infinite, whereas substitution by a moderate value gave a line I. The similarity of shapes between Figure S1 (a) and the line I implies that the obtained PL intensity can be used for quantitative analysis of glucose. The clarification of the reaction mechanism that determines the PL intensity including quantitative analysis of substrate using our ZAIS NCs chemosensor is under way and it will be reported in the future.