Supporting Information Available

Time-resolved probes and oxidase-based biosensors using terbium (III)/guanosine monophosphate/mercury (II) coordination polymer nanoparticles

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Experimental Section

Reagents and Materials. Terbium (III) nitrate hexahydrate was purchased from Diyang Chemical (Shanghai) Co. Ltd.. Glycine (Gly), alanine (Ala), valine (Val), leucine (Leu), isoleucine (Ile), proline (Pro), phenylalanine (Phe), tyrosine (Tyr), tryptophan (Trp), serine (Ser), threonine (Thr), cystine (Cys), methionine (Met), asparagine (Asn), glutarnine (Gln), asparticacid (Asp), glutamicacid (Glu), lysine (Lys), arginine (Arg), histidine (His), homocysteine (Hcys), oxidized glutathione (GSSG), reduced glutathione (GSH) and glucose oxidase (GOx) were purchased from Sigma-Aldrich (St. Louis, MO). Guanosine 5'-monophosphate disodium salt (GMP) was purchased from Sangon Biotech (Shanghai) Co. Ltd. Glucose was purchased from Qiangsheng Chemical (Jiangsu, China) Co. Ltd. 10×Tris-HAc buffer (100 mM, pH 7.9) was prepared using metal-free reagents in distilled water purified by a Milli-Q water purification system. All chemicals used in this work were of analytical reagent and obtained from commercial sources and directly used without additional purification.

Instrumentation. Luminescence spectra were measured in a luminescence microplate reader (infinite M200 pro, TECAN, Switzerland) using a black 384 well microplate (Fluotrac 200, Greiner, Germany). Photographs were taken with a digital camera. The excitation wavelength used was 290 nm for the emission spectra. For the time-resolved luminescence spectra, a delay time of 50 μs and a

gate time of 2 ms were used. The elemental analysis was performed with energy-dispersive X-ray spectrometer (EDX, X-Max Oxford, U.K.).

Preparation of Tb/GMP/Hg. Tb/GMP/Hg was prepared according to the reported method with minor modifications.[1] Briefly, l mL of $Tb(NO_3)_3$ aqueous solution (10 mM) and 0.5 mL of $Hg(Ac)_2$ aqueous solution (20 mM) were added to 0.5 mL of GMP disodium salt water solution (20 mM); white precipitate was formed immediately. The white precipitate was collected by centrifugation at 7000 rpm for 5 min. To remove unreacted reactants, we washed the precipitate with ultrapure water for several times. Finally, the obtained Tb/GMP/Hg was dispersed in 2 mL of Milli-Q water to form a Tb/GMP/Hg suspension.

Luminescence Response of Tb/GMP/Hg to Cys. To 10 μL of Tb/GMP/Hg suspension, 10 μL of different concentration of Cys solution and 10 μL Tris-HAc buffer (100 mM, pH 7.9) were added to make a final Cys concentration of 0, 10, 50, 100, 150, 200, 250, 300, 400, 500, 750 and 1000 μM, respectively; the total volume is 100 μL. The mixture was vortexed to mix all the reagents and then incubated for 10 min at room temperature and after that an aliquot of 100 μL mixture was placed in the black 384 well microplate to measure the luminescence intensity (excited at 290 nm, a delay time of 50 μs and a gate time of 2 ms). For the experiments of selectivity, 10 μL of stock solutions (1 mM) of Gly, Ala, Val, Leu, Ile, Pro, Phe, Tyr, Trp, Ser, Thr, Cys, Met, Asn, Gln, Asp, Glu, Lys, Arg, His, Hcy, GSSG and GSH and 10 μL Tris-HAc buffer (100 mM, pH 7.9) were added to 10 μL of Tb/GMP/Hg suspensions, respectively; the total volume reached to 100 μL. The mixture was vortexed to mix all the reagents and then incubated for 10 min at room temperature and after that an aliquot of 100 μL mixture was placed in the black 384 well microplate to measure the luminescence intensity (excited at 290 nm, a delay time of 50 μs and a gate time of 2 ms).

Assays for H_2O_2 using Tb/GMP/Hg-Cys sensing system. For H_2O_2 sensing, 10 μL of Tb/GMP/Hg suspension, 10 μL of 5 mM Cys solution and 10 μL Tris-HAc buffer (100 mM, pH 7.9) were mixed and then the mixture was treated with various H_2O_2 concentration of 0, 0.1, 0.5, 1, 2, 4, 6, 8, 10, 20, 40, 60, 80, 100, 200, 400, 600, 800 and 1000 μM, respectively; the total volume is 100 μL. The mixture was vortexed to mix all the reagents and then incubated for 20 min at room temperature and after that an aliquot of 100 μL mixture was placed in the black 384 well microplate to measure the luminescence intensity (excited at 290 nm, a delay time of 50 μs and a gate time of 2 ms).

Assays for glucose using Tb/GMP/Hg-Cys sensing system. For glucose sensing, 10 μL of Tb/GMP/Hg suspension, 10 μL of 5 mM Cys solution, 10 μL of 5 μM glucose oxidase (GOx) solution and 10 μL Tris-HAc buffer (100 mM, pH 7.9) were mixed and then the mixture was treated with various glucose concentration of 0, 0.1, 0.5, 1, 2, 4, 6, 8, 10, 20, 40, 60, 80, 100, 200, 400, 600, 800 and 1000 μM, respectively; the total volume is 100 μL. The mixture was vortexed to mix all the reagents and then incubated for 60 min at room temperature and after that an aliquot of 100 μL mixture was placed in the black 384 well microplate to measure the luminescence intensity (excited at 290 nm, a delay time of 50 μs and a gate time of 2 ms).

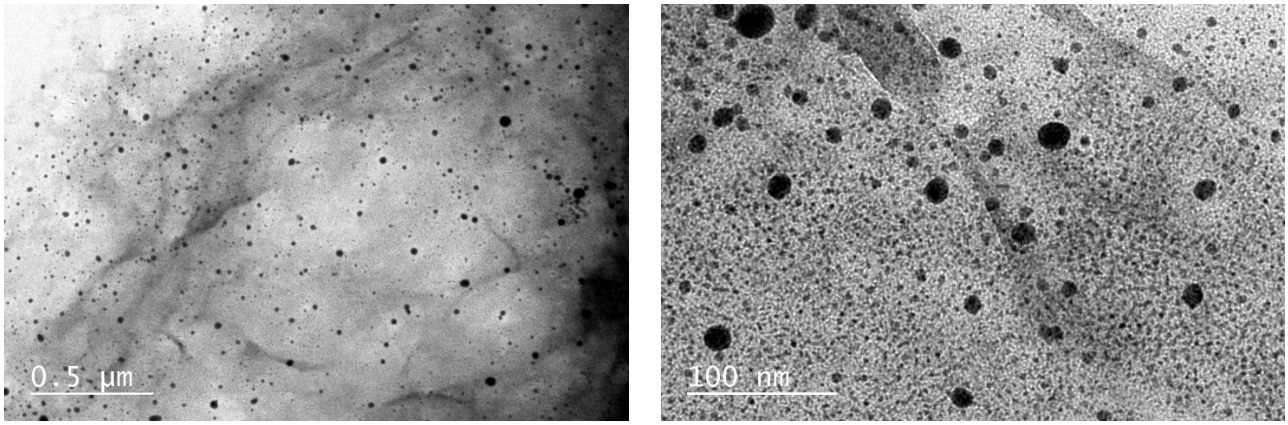

Figure S1 TEM images of Tb/GMP/Hg.

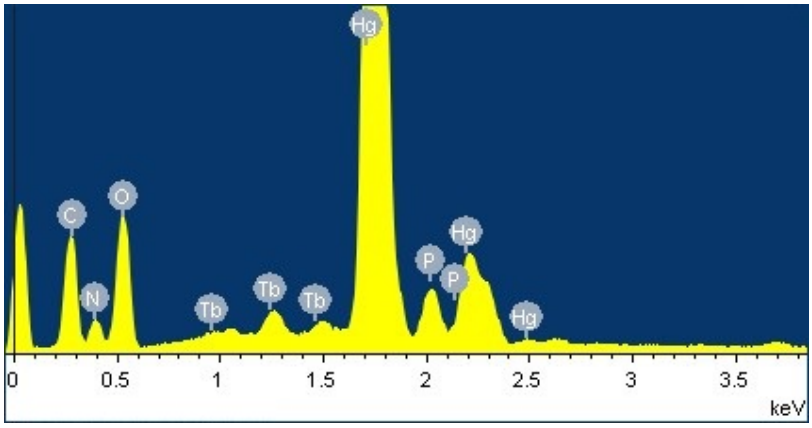

Figure S2 Energy-dispersive X-ray (EDX) spectra of Tb/GMP/Hg.

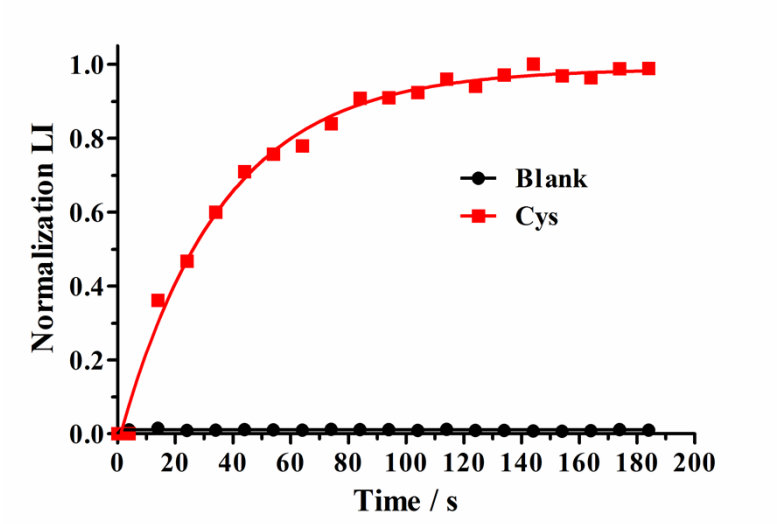

Figure S3 Kinetics investigation of luminescence response of Tb/GMP/Hg probe to 500 μM Cys.

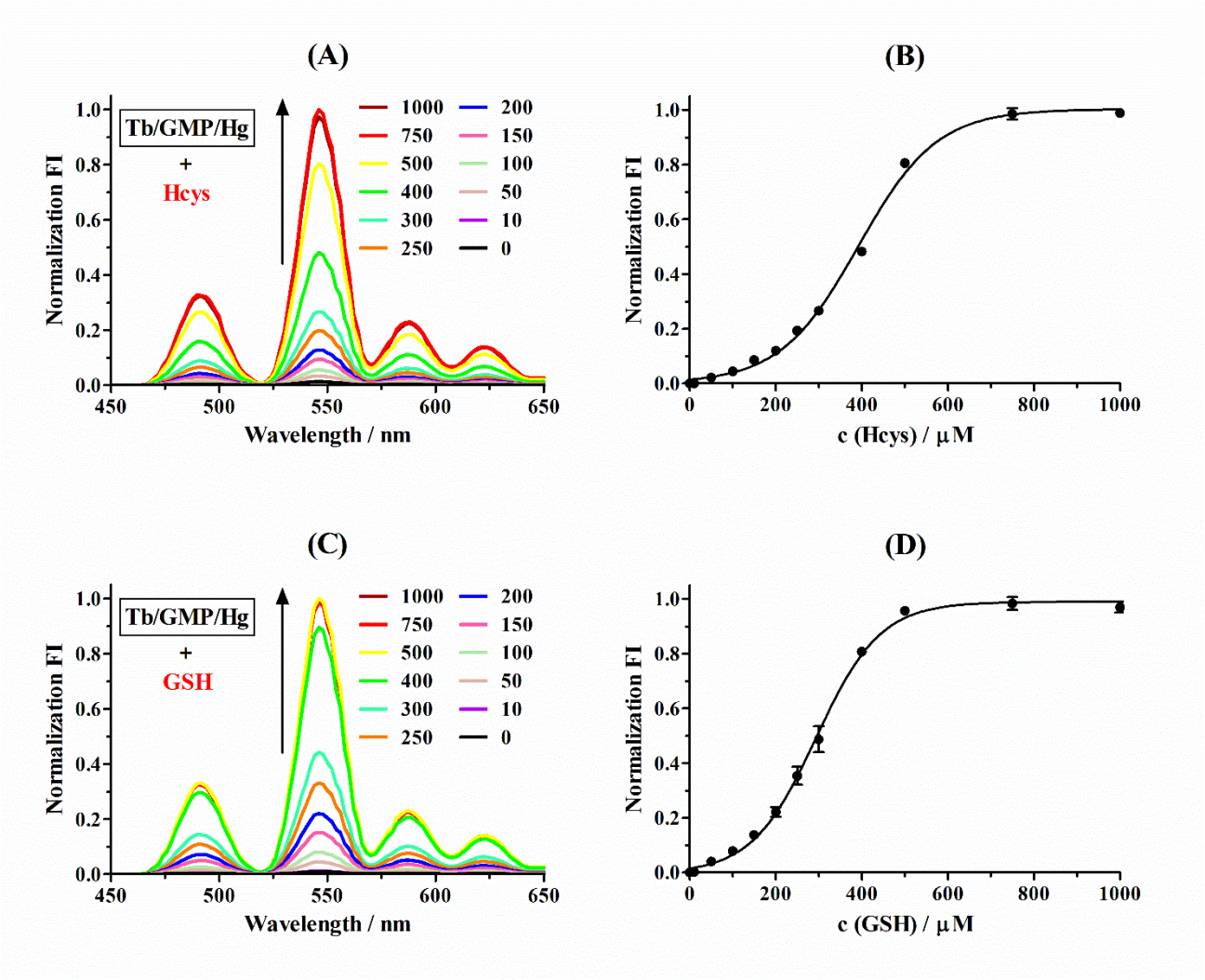

Figure S4 (a) Luminescence responses of the Tb/GMP/Hg probe to Hcys. The luminescence emission spectra are shown for various Hcys concentrations of 0, 10, 50, 100, 150, 200, 250, 300, 400, 500, 750 and 1000 μM; (b) Plot of luminescence responses of the Tb/GMP/Hg probe to the various concentrations of Hcys indicated; (c) Luminescence responses of the Tb/GMP/Hg probe to GSH. The luminescence emission spectra are shown for various GSH concentrations of 0, 10, 50, 100, 150, 200, 250, 300, 400, 500, 750 and 1000 μM; (d) Plot of luminescence responses of the Tb/GMP/Hg probe to the various concentrations of GSH indicated.

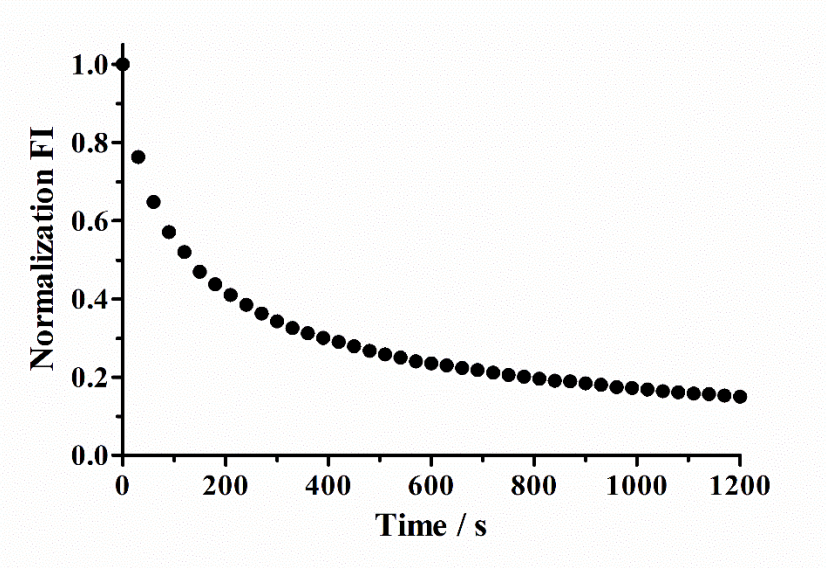

Figure S5 Kinetics investigation of luminescence response of the Tb/GMP/Hg-Cys sensing system (500 μM Cys used) to 1 mM H_2O_2.

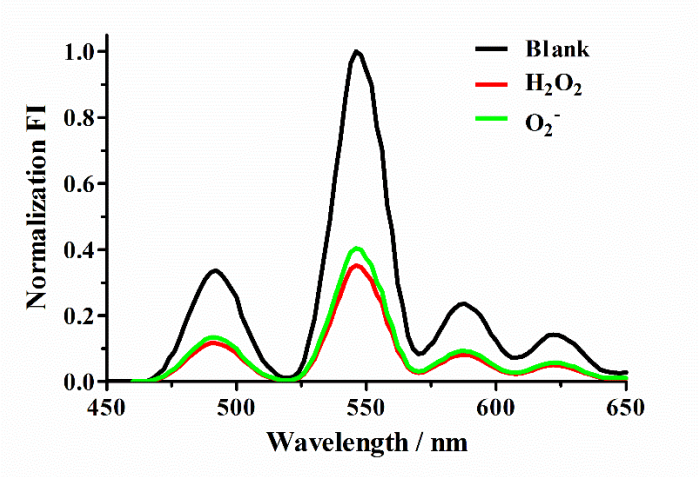

Figure S6 Luminescence responses of the Tb/GMP/Hg-Cys sensing system to 100 μM ROS including H_2O_2 and superoxide free radical (O_2^-). O_2^- generated from dissolved KO_2 (200 μM) in the dimethyl sulphoxide (DMSO) and the concentration of O_2^- was estimated to be the half concentration of KO_2.

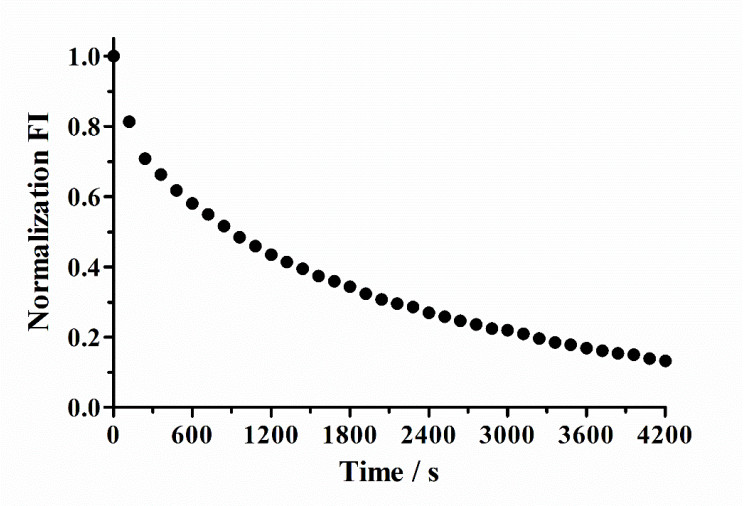

Figure S7 Kinetics investigation of luminescence response of the Tb/GMP/Hg-Cys-GOx sensing system (500 μM Cys and 0.5 μM GOx used) to 1 mM glucose.

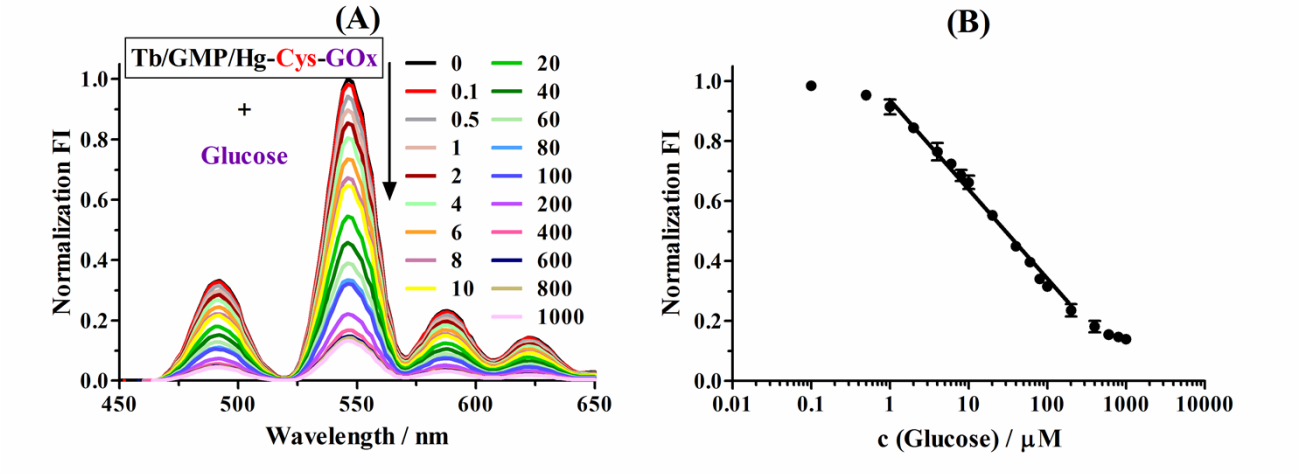

Figure S8. The determination of glucose using the Tb/GMP/Hg-Cys-GOx sensing system (500 μM Cys and 0.5 μM GOx used). (A) Luminescence responses of the Tb/GMP/Hg-Cys-GOx sensing system to various glucose concentrations of 0, 0.1, 0.5, 1, 2, 4, 6, 8, 10, 20, 40, 60, 80, 100, 200, 400, 600, 800 and 1000 μM; (B) Plot of luminescence responses of the Tb/GMP/Hg-Cys-GOx sensing system to various concentrations of glucose indicated.

References:

1. Nishiyabu, R.; Hashimoto, N.; Cho, T.; Watanabe, K.; Yasunaga, T.; Endo, A.; Kaneko, K.; Niidome, T.; Murata, M.; Adachi, C.; Katayama, Y.; Hashizume, M.; Kimizuka, N. *J. Am. Chem. Soc.* **2009**, *131*, 2151-2158.