Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information *for*

Optical and Electrochemical Responses of an Anthrax Biomarker Based on Single-Walled Carbon Nanotubes Covalently Loaded with Terbium Complexes

Chaoliang Tan [a], Qianming Wang [a*] and Cheng Cheng Zhang [b]

[a] *School of Chemistry and Environment, South China Normal University, Guangzhou 510006, P. R. China*

[b] *Departments of Physiology and Developmental Biology, University of Texas Southwestern Medical Center, Dallas, U S A*

* To whom the correspondence should be addressed. E-mail: qmwang@scnu.edu.cn

Tel: 86-20-39310258; Fax: 86-20-39310187

Experimental Section

All starting materials were obtained from commercial suppliers and used as received. Fluorescence spectra were measured on an Agilent 8453 spectrophotometer and an Edinburgh FLS920 spectrometer. Visible absorption spectra were obtained with an Agilent 8453 spectrophotometer. Fourier transform infrared spectra were measured by Prestige-21, Shimadzu. TEM was measured using a JEOL JEM-2100HR transmission electron microscope. SEM was measured using a Tescan 5136MM scanning electron microscope. Cyclic voltammetry was performed on a CHI660a electrochemical system with a corresponding software package. The carboxyl-modified single-walled carbon nanotube (SWNT-COOH) was obtained from Chengdu Organic Chemistry Co. Ltd. Bis(anthranilic acid) was prepared according to a previously published method.[1]

The preparation of bis(anthranilic acid)-modified SWNT (SWNT-2)

SWNT-COOH (SWNT-1, 100 mg) was stirred in 20 mL of $SOCl_2$ containing 0.5 mL of DMF at 70℃ for 24 h.[2] After centrifugation, the brown-colored supernatant was decanted and the remaining solid was washed with anhydrous THF. After centrifugation, the pale yellow colored supernatant was decanted. The remaining solid was dried at room temperature under vacuum, giving acyl chloride-modified SWNT (SWNT-1f).

A mixture of 100 mg of SWNT-1f and 60 mg of bis(anthranilic acid) in 10 mL dry THF was heated at ～100℃ for 96 h.[2] After the mixture was cooled to room temperature, solvent was evaporated under vacuum. After washing with ethanol four times (5 to 10 min sonication with each wash), the remaining solid was dissolved in ethanol to remove excess bis(anthranilic acid). The suspension was centrifuged and the black precipitate was washed twice with THF. The resulting bis(anthranilic acid)-modified SWNT-2 was dried at room temperature under vacuum.

Synthesis of terbium complex-modified SWNT (SWNT-3)

SWNT-2 (50 mg) and $Tb(NO_3)_3 \cdot 6H_2O$ (50 mg) were dissolved in 15 mL ethanol, 3~5 drops of aq. $NH_3 \cdot H_2O$ were added, and the solution was refluxed for 5 h. After centrifugation,

the precipitate was washed with ethanol twice and dried at room temperature under vacuum to yield SWNT-3.

The preparation of working electrodes assembled with SWNT-2 and SWNT-3

SWNT-2 (30 mg) or SWNT-3 (30 mg), poly(vinylidene fluoride) (PVDF, 3 mg), and 3~5 drops of N-methyl-2-pyrrolidone were mixed in a mortar and ground into a homogeneous mixture. The mixture was homogeneously coated onto a rectangular (1 cm × 5 cm) steel wire mesh (1 mm × 2 mm) and dried for 3 days at room temperature. The electrode properties were tested in a three-electrode system using the prepared electrodes as working electrode, Pt as the auxiliary electrode, Hg/Hg_2SO_4 as the reference electrode, and 1 mol/L Na_2SO_4 solution as electrolyte.

1 M. C. Tseng, C. Y. Lai, Y. W. Chu, Y. H. Chu, *Chem. Commun.*, 2009, **4**, 445.

2 Y. P. Sun, K. F. Fu, Y. Lin, W. J. Huang, *Acc. Chem. Res.*, 2002, **35**, 1096.

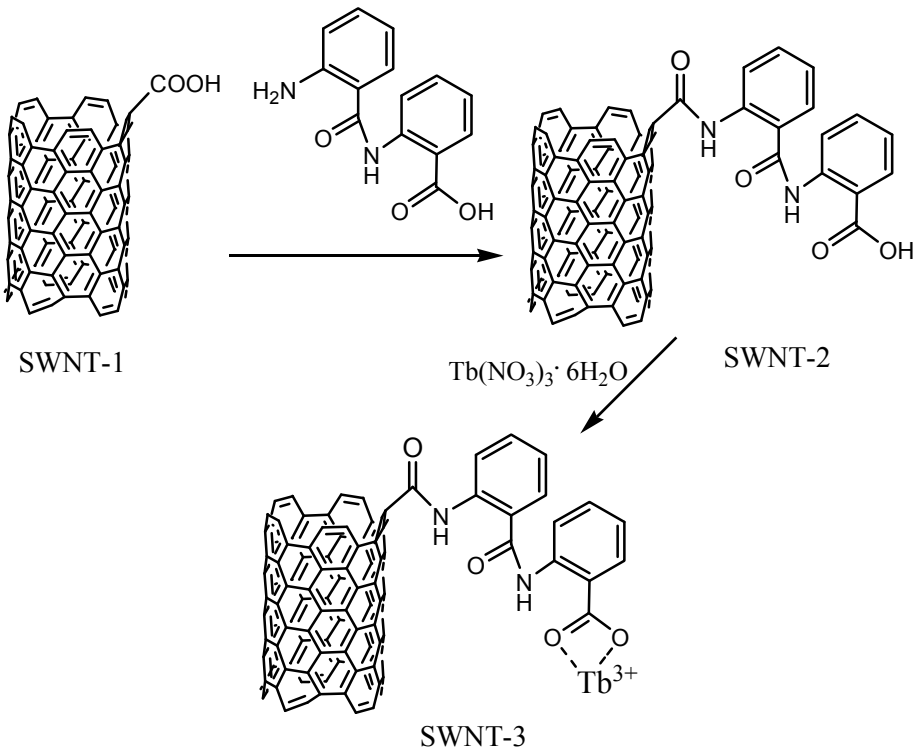

Fig. S1 Synthetic Scheme for SWNT-3

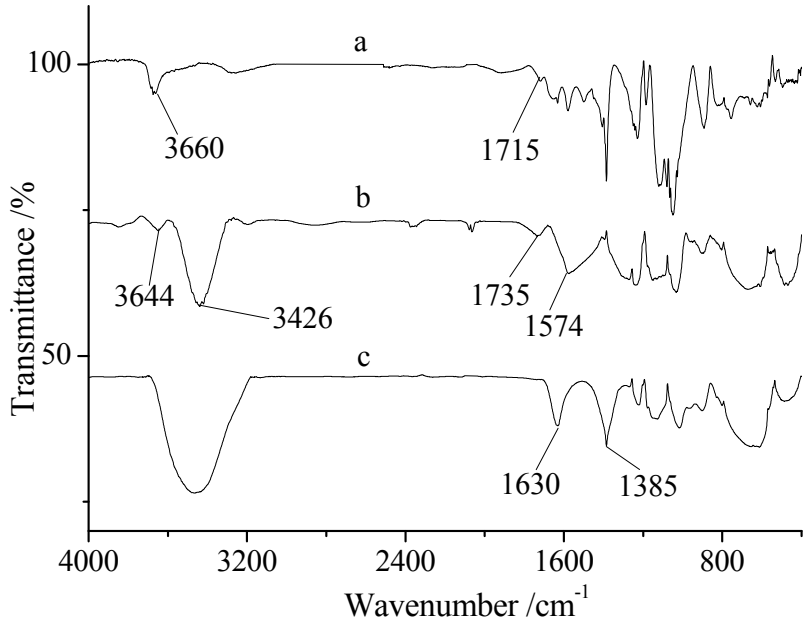

Fig. S2 IR spectra of (a) SWNT-1, (b) SWNT-2, and (c) SWNT-3.

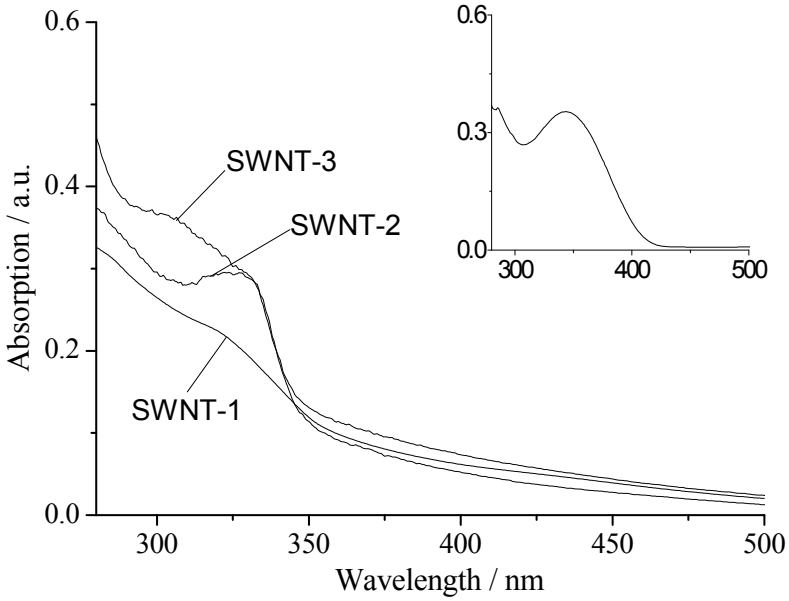

Fig. S3 UV-vis spectra of the SWNT-1, SWNT-2 and SWNT-3. Inset: UV-vis spectrum of bis(anthranilic acid). Spectra were recorded in DMSO as solvent at 1 mg/L.

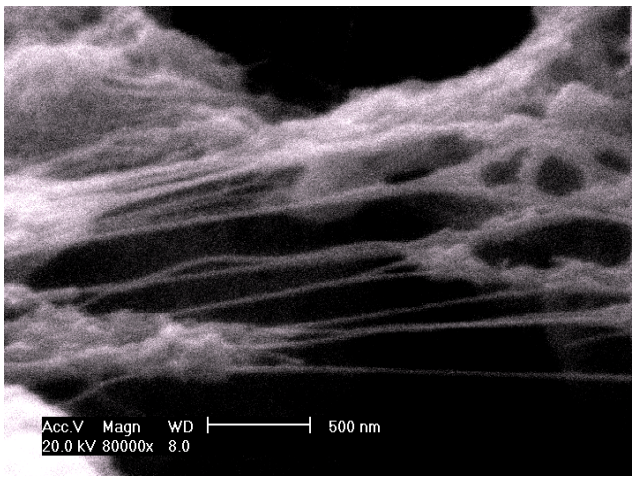

Fig. S4 Scanning electric microscopy of SWNT-3.

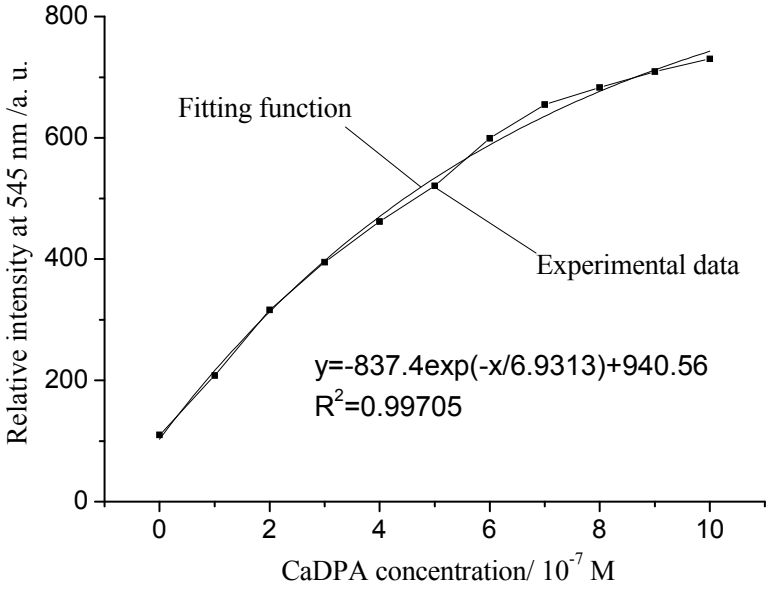

Fig. S5 Relative intensity of SWNT-3 at 545 nm with the concentration over a CaDPA concentration range from 10^{-7} to 10^{-6} M.

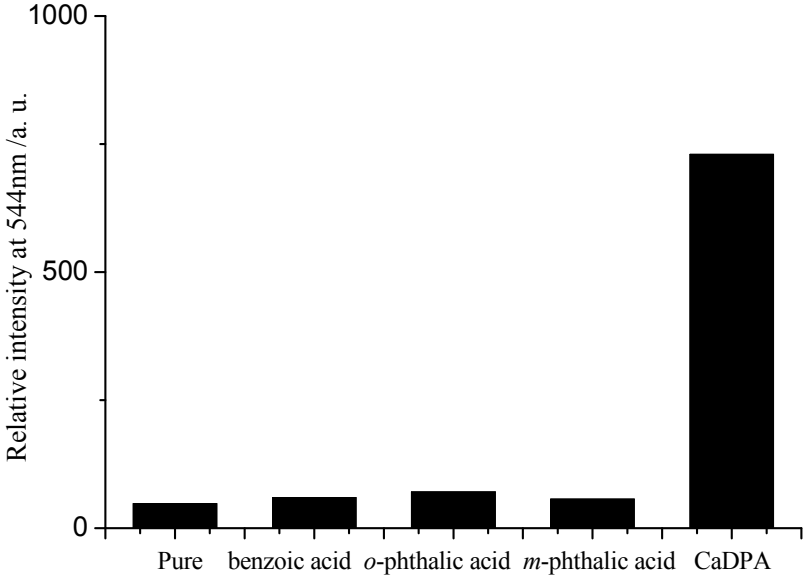

Fig. S6 Emission spectra of SWNT-3 (1 mg/L in DMSO) excited at 395 nm in the presence of 10^{-5} mol/L of benzoic acid, *o*-phthalic acid, *m*-phthalic acid, or CaDPA.

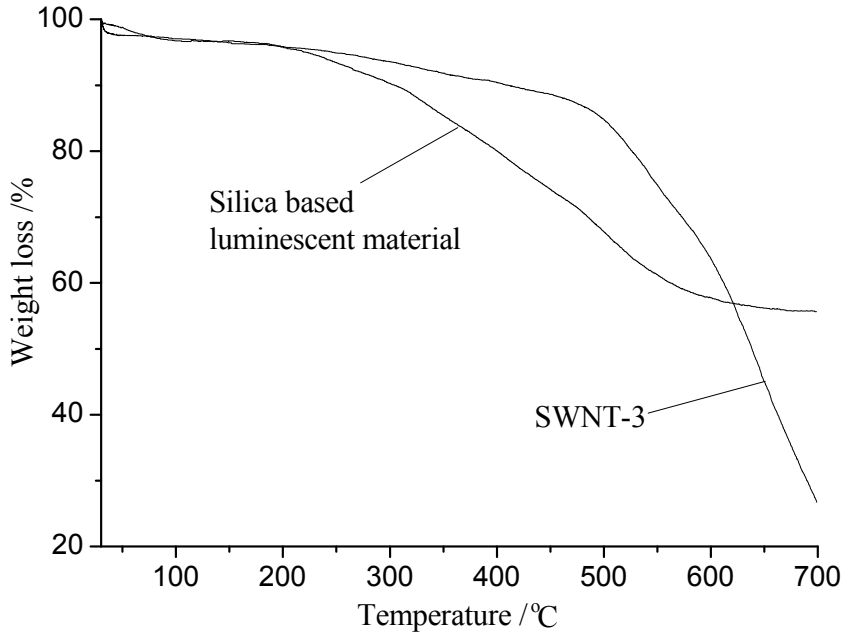

Fig. S7 Thermogravimetric analysis traces of SWNT-3 and silica-based luminescent material.

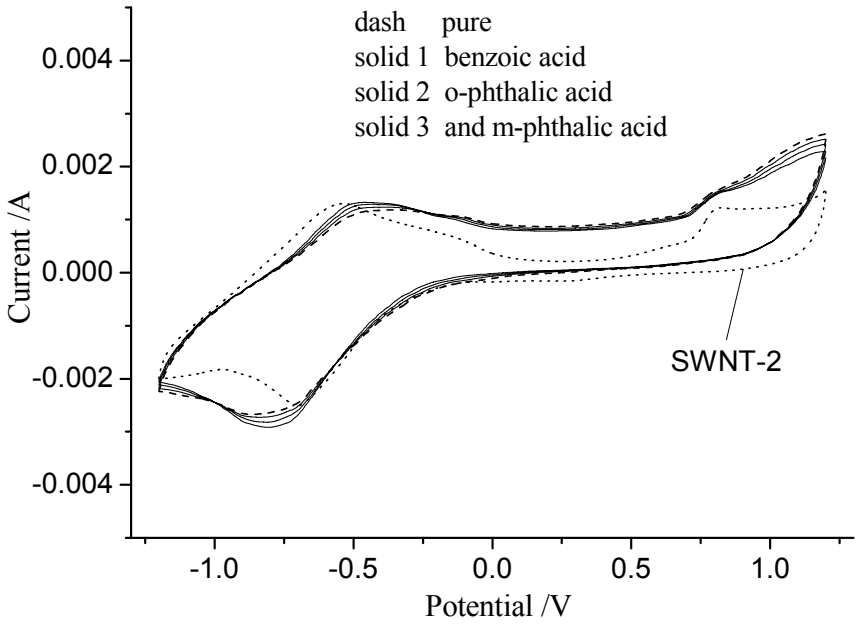

Fig. S8 Cyclic voltammograms of SWNT-3 assembled on an electrode with and without 10^{-5} M benzoic acid, *o*-phthalic acid, or *m*-phthalic acid and cyclic voltammogram of SWNT-2 assembled on an electrode.