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Supporting Information for

Hybrid Silica Nanoparticles for Luminescent Spore Detection

Kathryn M. L. Taylor and Wenbin Lin*

Department of Chemistry, CB#3290, University of North Carolina, Chapel Hill, NC 27599, USA

Nanoparticle Synthesis

Synthesis of monoAPS-EDTA-Tb coated silica nanoparticles. MonoAPS-EDTA-Tb coated silica nanoparticles were synthesized using a Triton-X100/1-hexanol/cyclohexane/water microemulsion system. To 50 mL of a 0.3 M Triton-X100/1.5 M 1-hexanol/cyclohexane solution was added, 3.05 mL of distilled water and 0.50 mL of tetraethylorthosilicate (TEOS). The mixture was stirred for 10 minutes at room temperature to allow for the formation of a microemulsion with a *W*-value of 15. 1 mL of aqueous ammonia was then added to initiate the hydrolysis. After stirring for 24 hours, 75 µL of a 0.0176 M aqueous solution of monoAPS-EDTA-Tb (**1**) was added to 25 mL of the reaction mixture. The reaction was then stirred for an additional 16 hours at room temperature. 25 mL of ethanol was added to the reaction to precipitate the particles which were then collected by centrifuging at 13500 rpm for 20 minutes. The particles were then washed twice with ethanol and once with water before being redispersed in 5 mL of distilled water. Yield = 53 mg

Synthesis bisAPS-EDTA-Tb coated silica nanoparticles. BisAPS-EDTA-Tb coated silica nanoparticles were synthesized using a Triton-X100/1-hexanol/cyclohexane/water microemulsion system. To 20 mL of a 0.3 M Triton-X100/1.5 M 1-hexanol/cyclohexane solution was added, 1.22 mL of distilled water and 0.20 mL of tetraethylorthosilicate (TEOS). The mixture was stirred for 10 minutes at room temperature to allow for the formation of a microemulsion with a *W*-value of 15. 0.4 mL of aqueous ammonia was then added to initiate the hydrolysis. After stirring for 24 hours, 42 µL of a 0.0313 M aqueous solution of bisAPS-EDTA-Tb (**2**) was added to the reaction mixture. The reaction was then stirred for an additional 18 hours at room temperature. 20 mL of ethanol was added to the reaction to precipitate the particles which were then collected by centrifuging at 13500 rpm for 20 minutes. The particles were then washed twice with ethanol and once with water before being redispersed in 5 mL of distilled water.

Synthesis of pentylamide-APS-EDTA-Tb coated silica nanoparticles. Pentylamide-APS-EDTA-Tb coated silica nanoparticles were synthesized using a Triton-X100/1-hexanol/cyclohexane/water microemulsion system. To 50 mL of a 0.3 M Triton-X100/1.5 M 1-hexanol/cyclohexane solution was added, 3.05 mL of distilled water and 0.50 mL of tetraethylorthosilicate (TEOS). The mixture was stirred for 10 minutes at

room temperature to allow for the formation of a microemulsion with a *W*-value of 15. 1 mL of aqueous ammonia was then added to initiate the hydrolysis. After stirring for 24 hours, 60 µL of a 0.0223 M aqueous solution of pentylamide-APS-EDTA-Tb (**3**) was added to 25 mL of the reaction mixture. The reaction was then stirred for an additional 16 hours at room temperature. 25 mL of ethanol was added to the reaction to precipitate the particles which were then collected by centrifuging at 13500 rpm for 20 minutes. The particles were then washed twice with ethanol and once with water before being redispersed in 5 mL of distilled water.

Synthesis monoAPS-EDTA-Tb coated, $Ru(bpy)_3^{2+}$ doped, silica nanoparticles. MonoAPS-EDTA-Tb coated, $Ru(bpy)_3^{2+}$ doped, silica nanoparticles were synthesized using a Triton-X100/1-hexanol/cyclohexane/water microemulsion system. To 10 mL of a 0.3 M Triton-X100/1.5 M 1-hexanol/cyclohexane solution was added, 0.57 mL of distilled water, 40 µL of a 0.1 M $Ru(bpy)_3^{2+}$ aqueous solution, and 0.10 mL of tetraethylorthosilicate (TEOS). The mixture was stirred for 10 minutes at room temperature to allow for the formation of a microemulsion with a *W*-value of 15. 0.2 mL of aqueous ammonia was then added to initiate the hydrolysis. After stirring for 24 hours, 28 µL of a 0.0176 M aqueous solution of monoAPS-EDTA-Tb (**1**) was added to the reaction mixture. The reaction was then stirred for an additional 18 hours at room temperature. 10 mL of methanol was added to the reaction to precipitate the particles which were then collected by centrifuging at 13500 rpm for 20 minutes. The particles were then washed twice with ethanol and once with water before being redispersed in 1.5 mL of distilled water.

Synthesis bisAPS-EDTA-Tb coated, $Ru(bpy)_3^{2+}$ doped, silica nanoparticles. BisAPS-EDTA-Tb coated, $Ru(bpy)_3^{2+}$ doped, silica nanoparticles were synthesized using a Triton-X100/1-hexanol/cyclohexane/water microemulsion system. To 10 mL of a 0.3 M Triton-X100/1.5 M 1-hexanol/cyclohexane solution was added, 0.57 mL of distilled water, 40 µL of a 0.1 M $Ru(bpy)_3^{2+}$ aqueous solution, and 0.10 mL of tetraethylorthosilicate (TEOS). The mixture was stirred for 10 minutes at room temperature to allow for the formation of a microemulsion with a *W*-value of 15. 0.2 mL of aqueous ammonia was then added to initiate the hydrolysis. After stirring for 24 hours, 16 µL of a 0.0313 M aqueous solution of bisAPS-EDTA-Tb (**2**) was added to the reaction mixture. The reaction was then stirred for an additional 18 hours at room temperature. 10 mL of methanol was added to the reaction to precipitate the particles which were then collected by centrifuging at 13500 rpm for 20 minutes. The particles were then washed twice with ethanol and once with water before being redispersed in 1.5 mL of distilled water.

Reloading of Tb into Coated Nanoparticles. The terbium was reloaded into the EDTA coated nanoparticles using the following procedure. The nanoparticles were suspended in distilled water, and the pH was measured to be approximately 9.5. An aqueous solution of $TbCl_3$ was then added, and the suspension was stirred at room temperature for 16 hours. The amount of $TbCl_3$ added was equal to the amount of Tb complex initially added during the particle synthesis. The particles were then isolated by

centrifuging at 13500 rpm for 25 minutes, and were washed twice with distilled water to remove any excess Tb. The particles were then dispersed in 2.5 mL of distilled water.

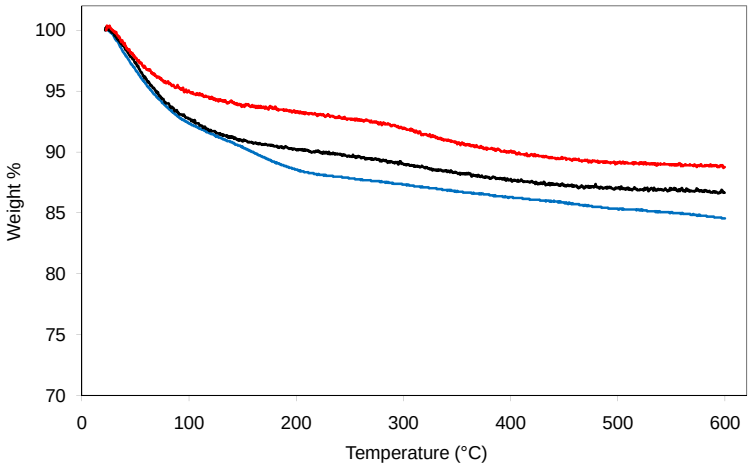

Figure S1. TGA of silica nanoparticles coated with complexes **1** (black), **2** (red), and **3** (blue).

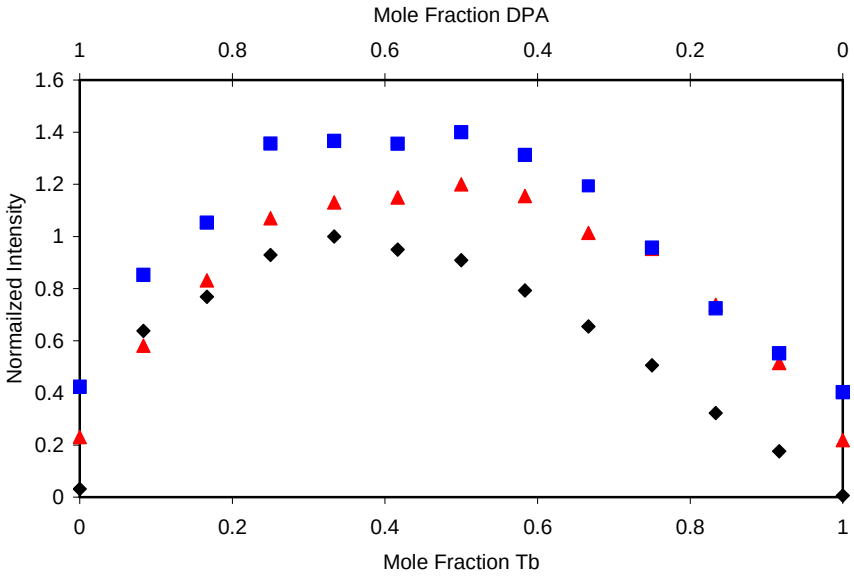

Figure S2. Job's plots of Tb complexes **1** (black diamonds), **2** (red triangles), and **3** (blue squares). The curves for complexes **2** and **3** are offset by 0.2 and 0.4 normalized intensity units, respectively.

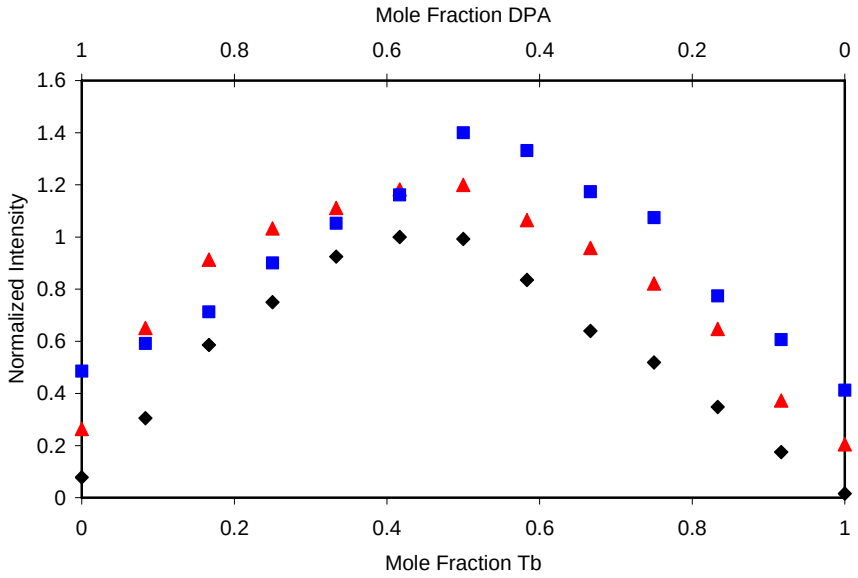

Figure S3. Job's plots of nanoparticle sensors functionalized with complexes **1** (black diamonds), **2** (red triangles), and **3** (blue squares). The curves for sensors functionalized with complexes **2** and **3** are offset by 0.2 and 0.4 normalized intensity units, respectively.

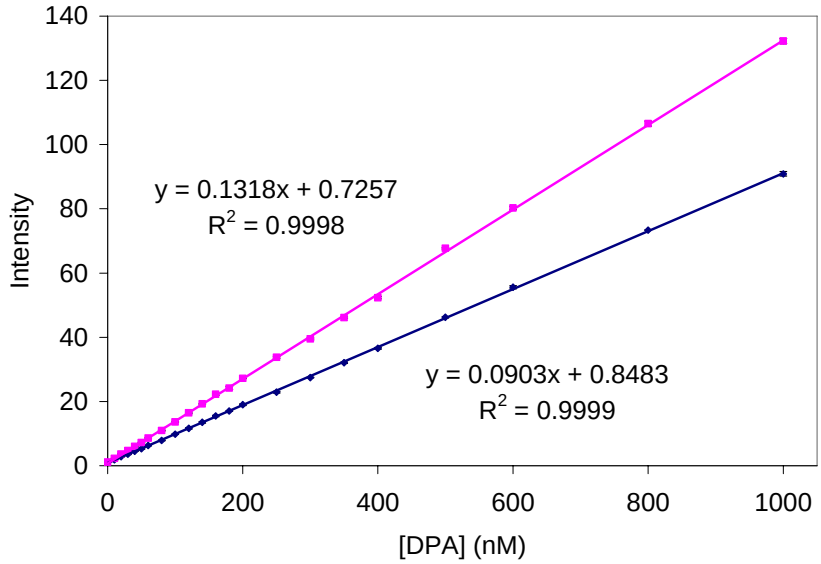

Figure S4. Calibration curve for DPA detection using a 10 µM solution of free monoAPS-EDTA-Tb complex (**1**) obtained by plotting the intensity at 489 nm (blue) and 544 nm (pink) vs. [DPA]. The detection limit was calculated to be 5.02 nM using the peak at 489 nm and 4.12 nM using the peak at 544 nm.

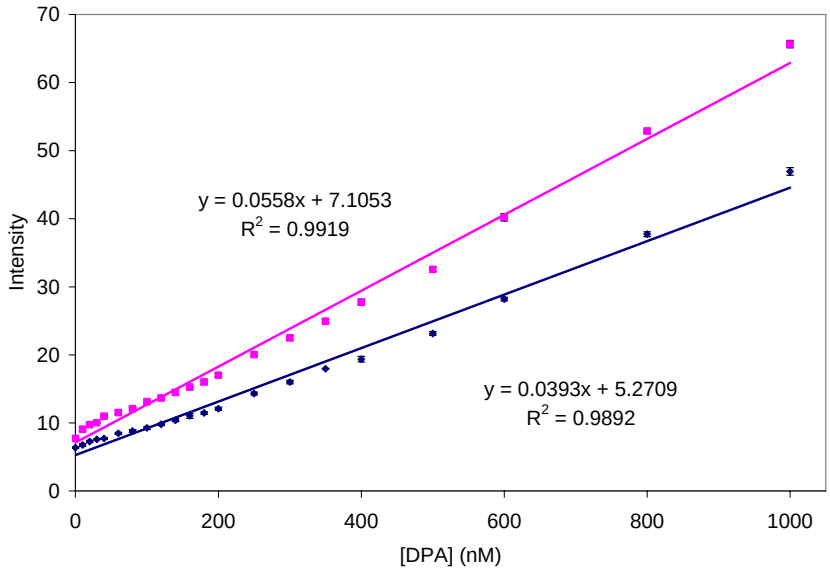

Figure S5. Calibration curve for DPA detection using a suspension of monoAPS-EDTA-Tb (**1**) coated particles with a Tb concentration of 10 µM obtained by plotting the intensity at 489 nm (blue) and 544 nm (pink) vs. [DPA]. The detection limit was calculated to be 34.6 nM using the peak at 489 nm and 15.7 nM using the peak at 544 nm.

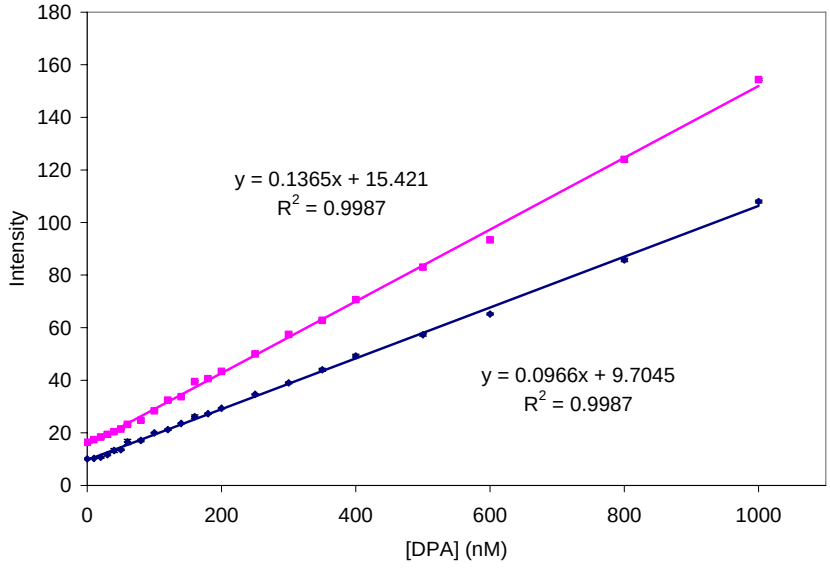

Figure S6. Calibration curve for DPA detection using a 10 µM solution of free bisAPS-EDTA-Tb (**2**) complex obtained by plotting the intensity at 489 nm (blue) and 544 nm (pink) vs. [DPA]. The detection limit was calculated to be 7.11 nM using the peak at 489 nm and 9.39 nM using the peak at 544 nm.

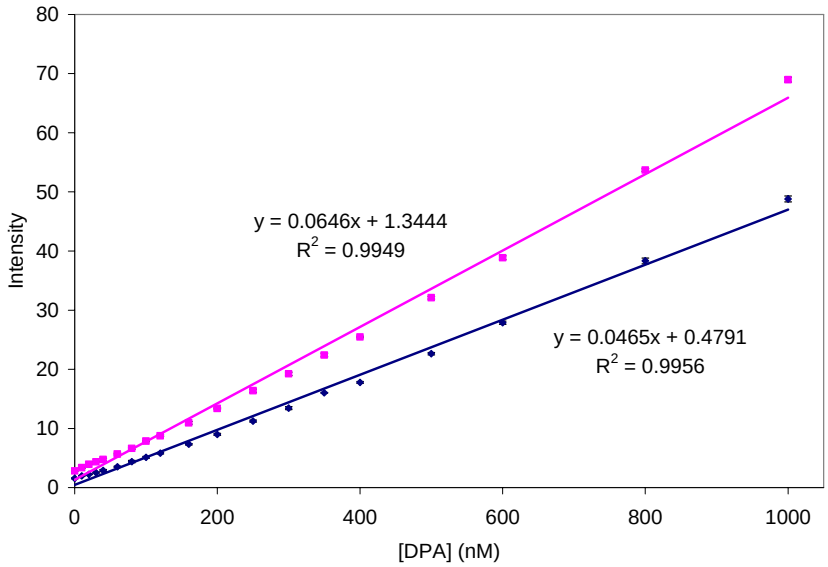

Figure S7. Calibration curve for DPA detection using a suspension of pentylamide-APS-EDTA-Tb (**3**) coated particles with a Tb concentration of 10 µM obtained by plotting the intensity at 489 nm (blue) and 544 nm (pink) vs. [DPA]. The detection limit was calculated to be 27.2 nM using the peak at 489 nm and 24.1 nM using the peak at 544 nm.