

Supporting Information for

“Off–On–Off” Fluorescent Chemosensor for pH Measurement with Terbium(III) Complex Based on a Tripodal Salicylic-Acid Derivative

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1. ^1H , ^{13}C NMR and ESI-MS plots of the compound 2.

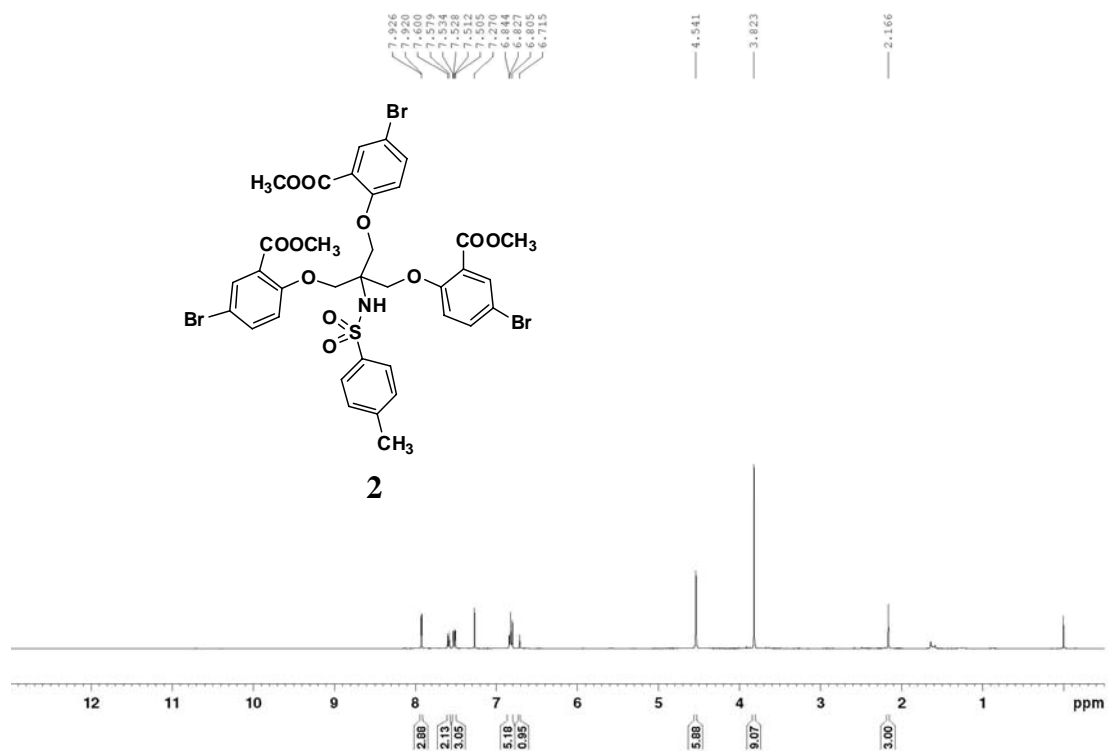


Figure S1. ^1H NMR (CDCl_3 , 400 MHz) spectrum of 2.

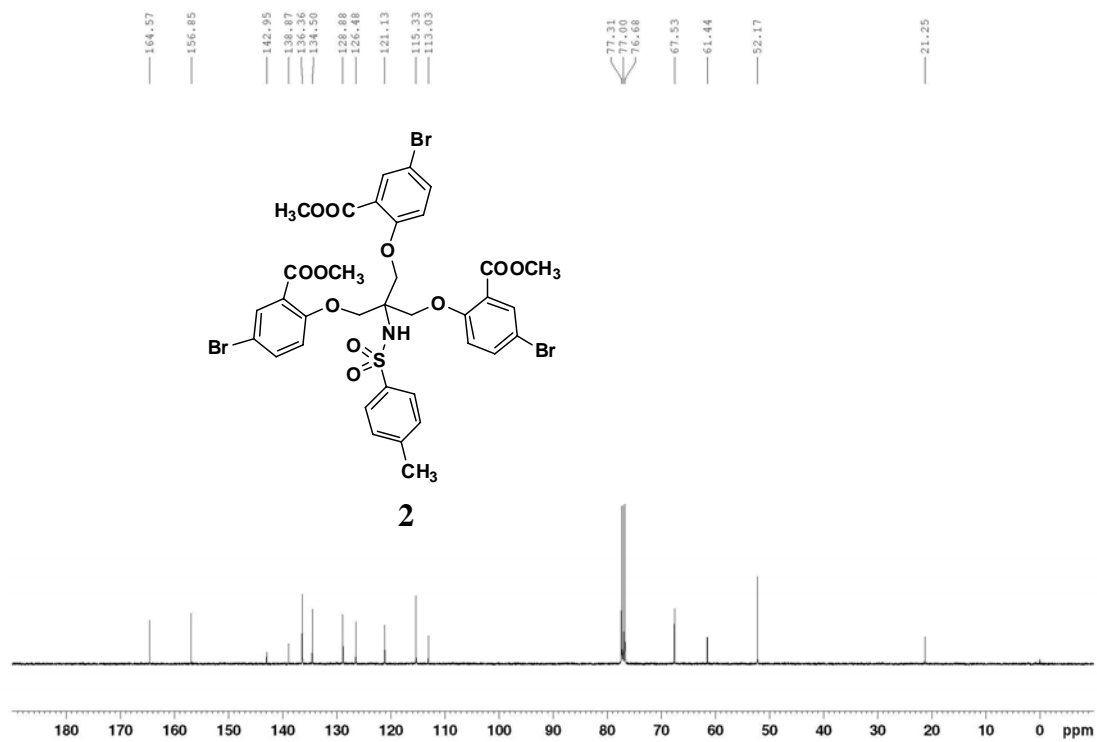


Figure S2. ^{13}C NMR (CDCl₃, 100 MHz) spectrum of **2**.

Generic Display Report

Analysis Info

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Sample Name M=910 914.
Comment

Acquisition Date 6/17/2010 3:52:16 PM

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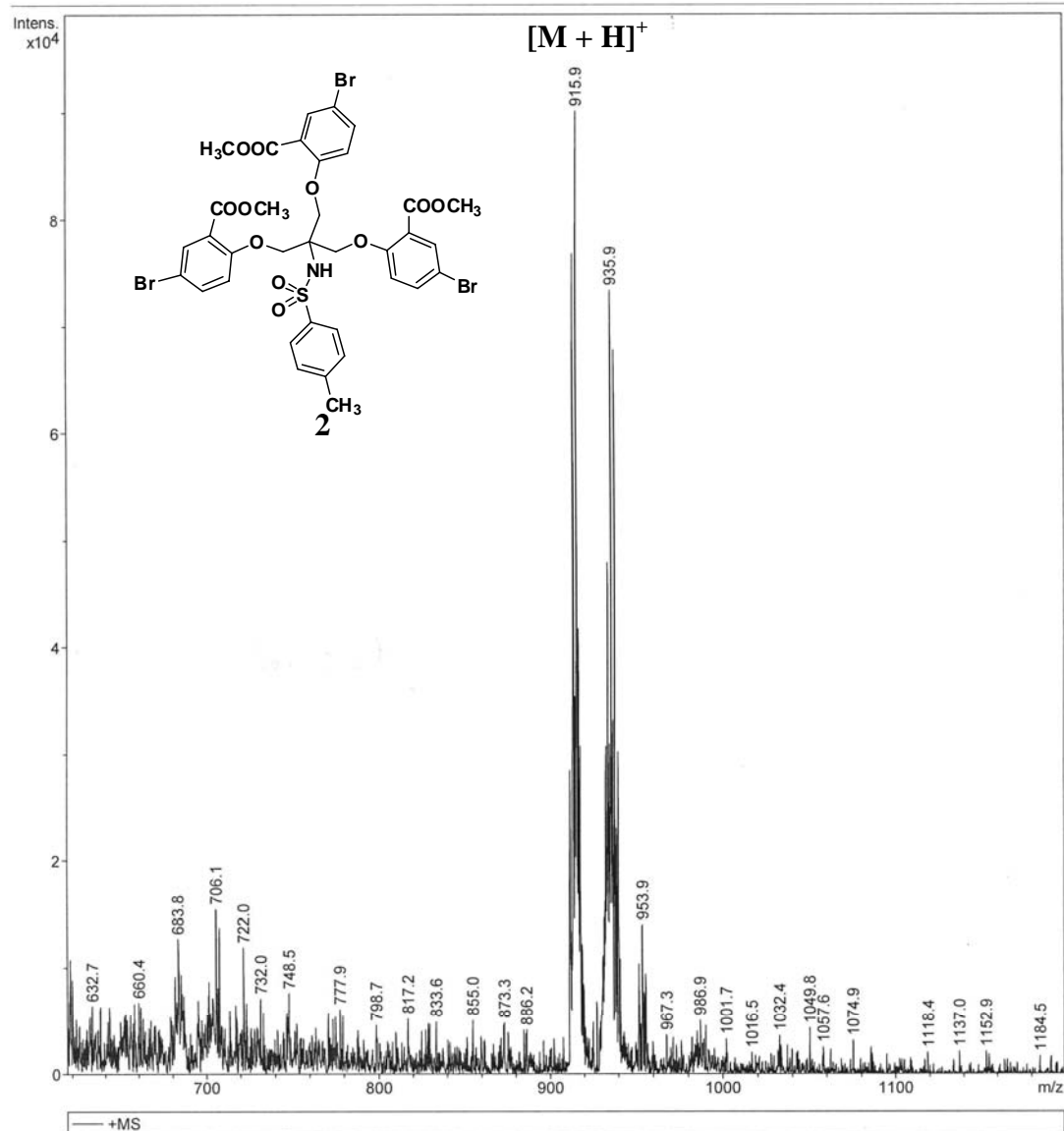


Figure S3. ESI mass spectrum of 2.

2. ^1H , ^{13}C NMR, IR, and HRMS plots of the probe H_3BSA .

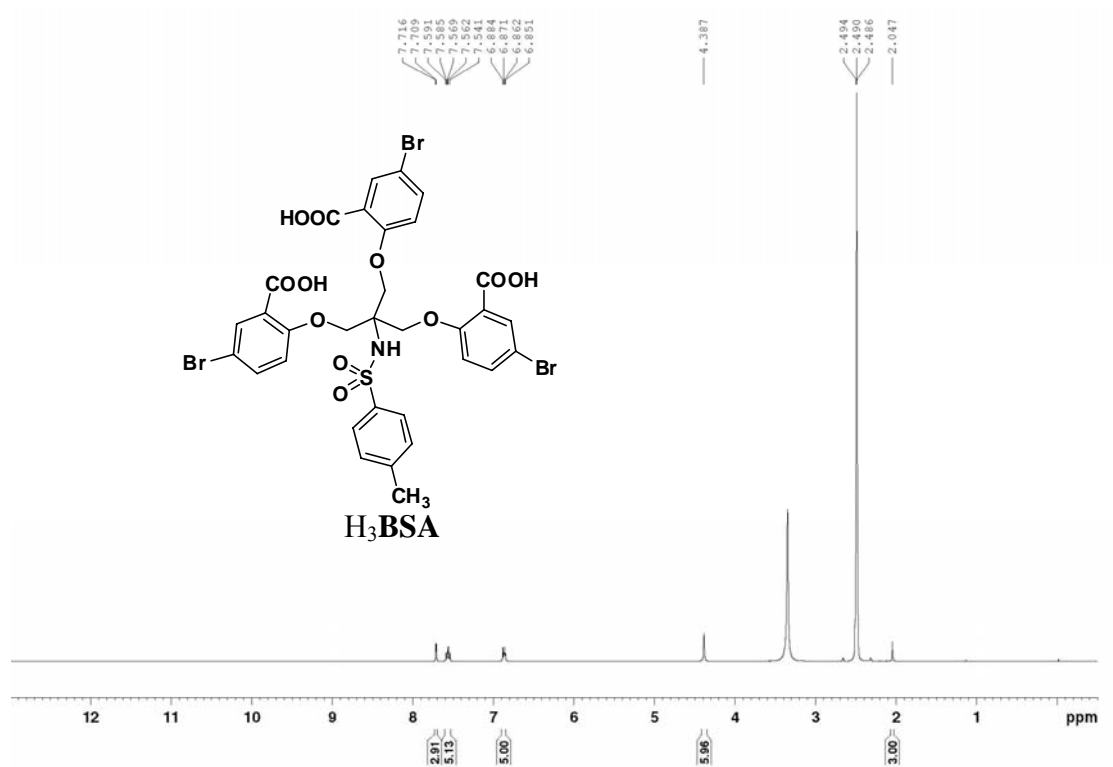


Figure S4. ^1H NMR ($\text{DMSO-}d_6$, 400 MHz) spectrum of H_3BSA .

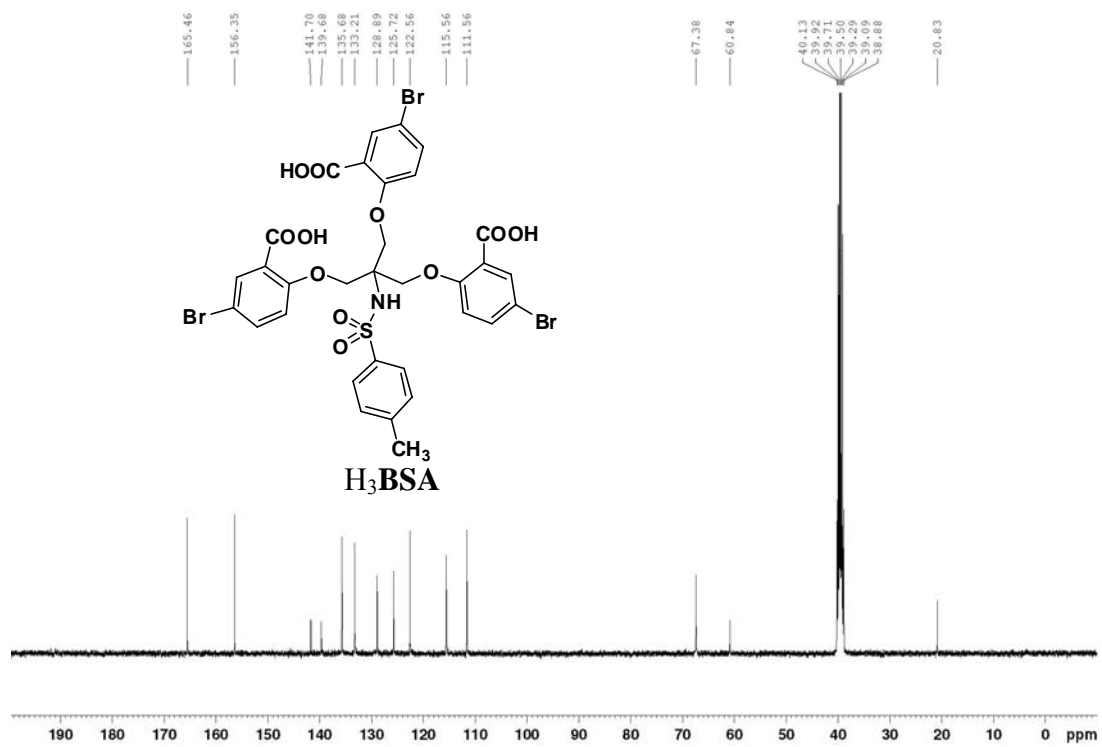


Figure S5. ¹³C NMR (DMSO-*d*₆, 100 MHz) spectrum of H₃BSA.

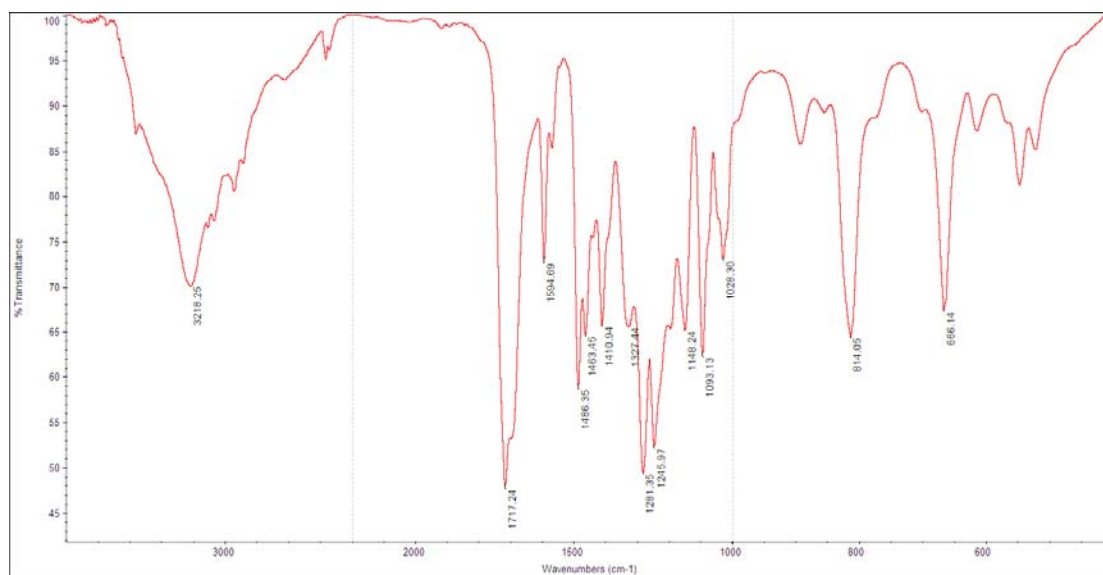


Figure S6. IR spectrum of H₃BSA.

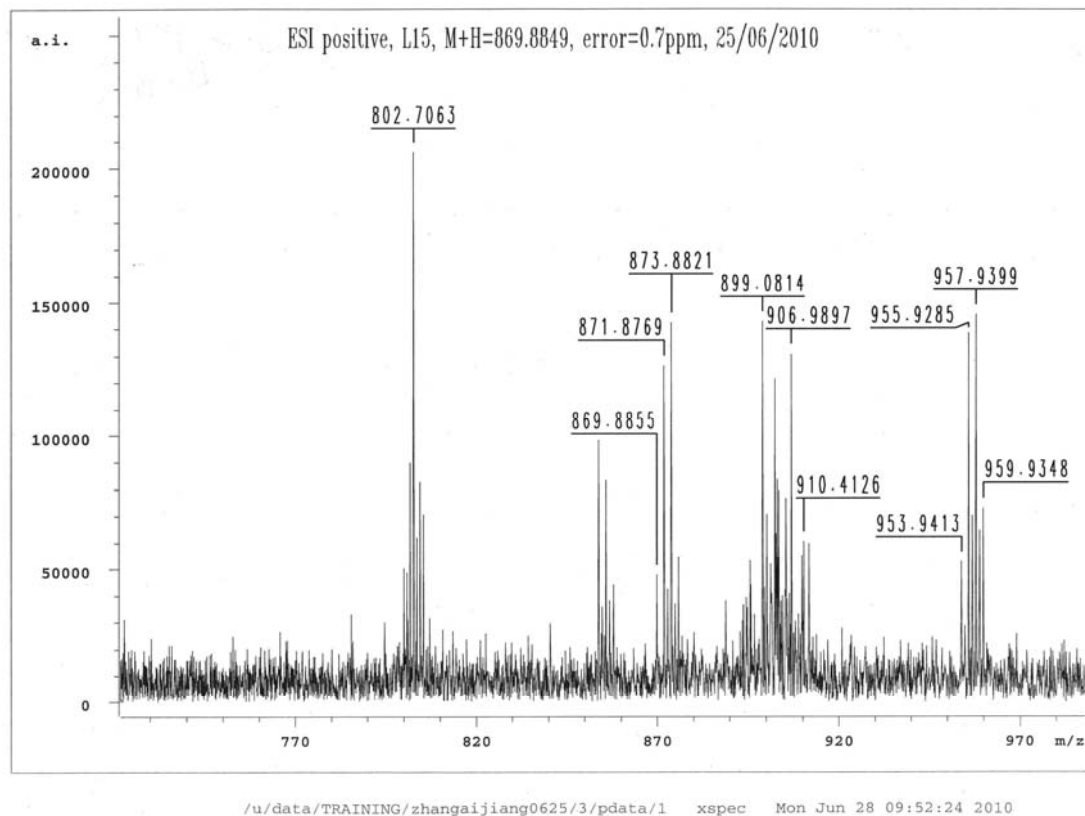


Figure S7. HRMS of H₃BSA.

3. IR plots of BSA•Eu, BSA•Gd and BSA•Tb.

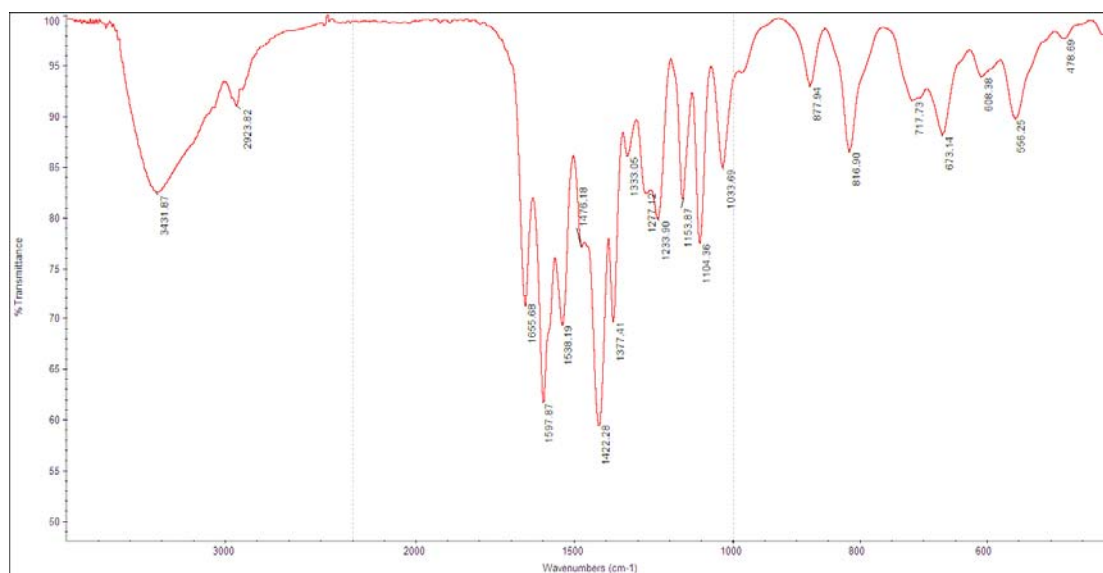


Figure S8. IR spectrum of BSA•Eu.

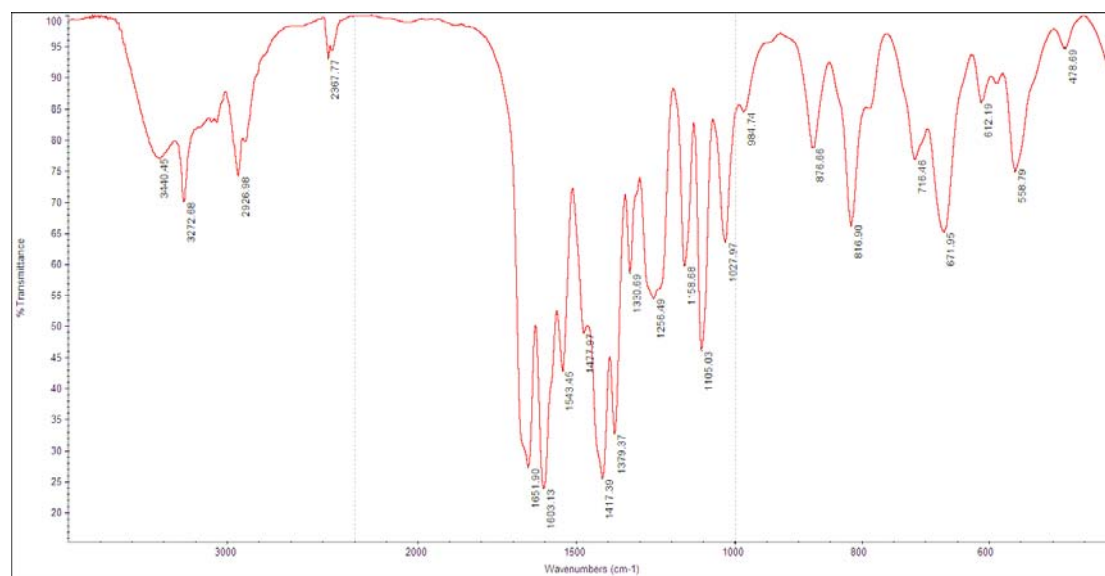


Figure S9. IR spectrum of BSA•Gd.

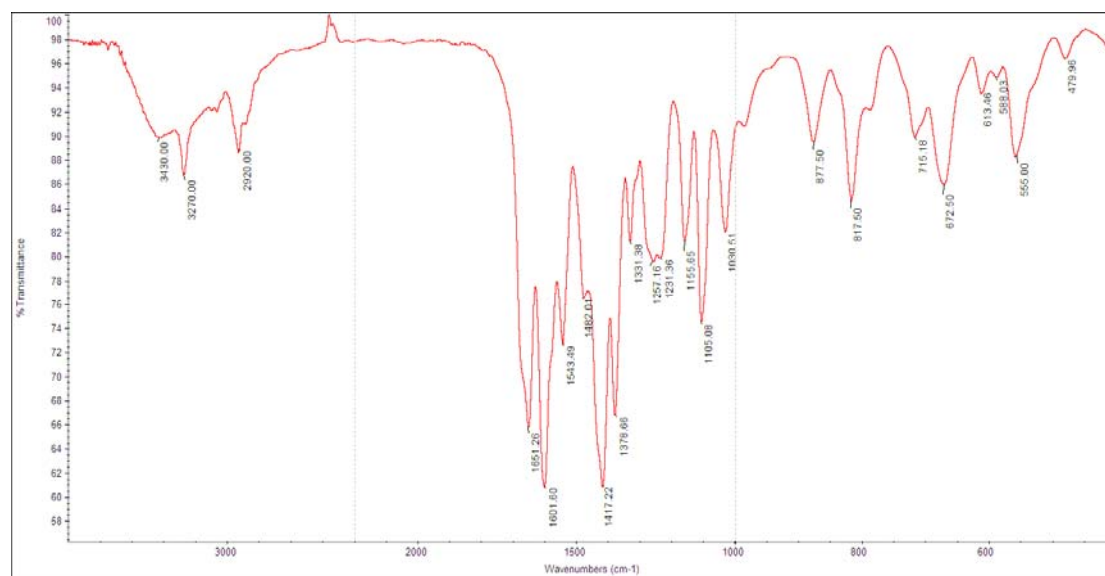


Figure S10. IR spectrum of **BSA•Tb**.

4. UV-visible absorption spectrum of H₃BSA in Tris-buffer.

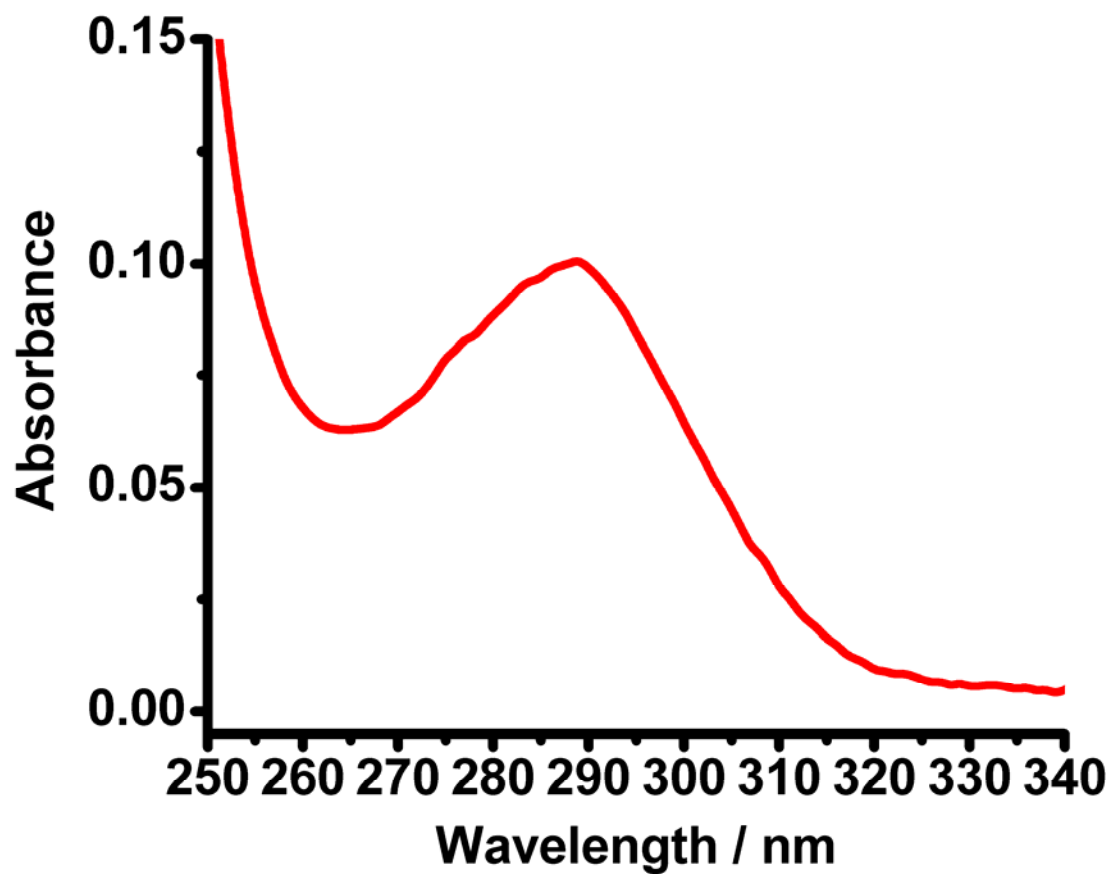


Figure S11. UV-visible absorption spectrum of H₃BSA in Tris-buffer (1% DMSO, v/v) solution (1.0×10^{-5} M).

5. Phosphorescence spectrum of BSA•Gd at 77K.

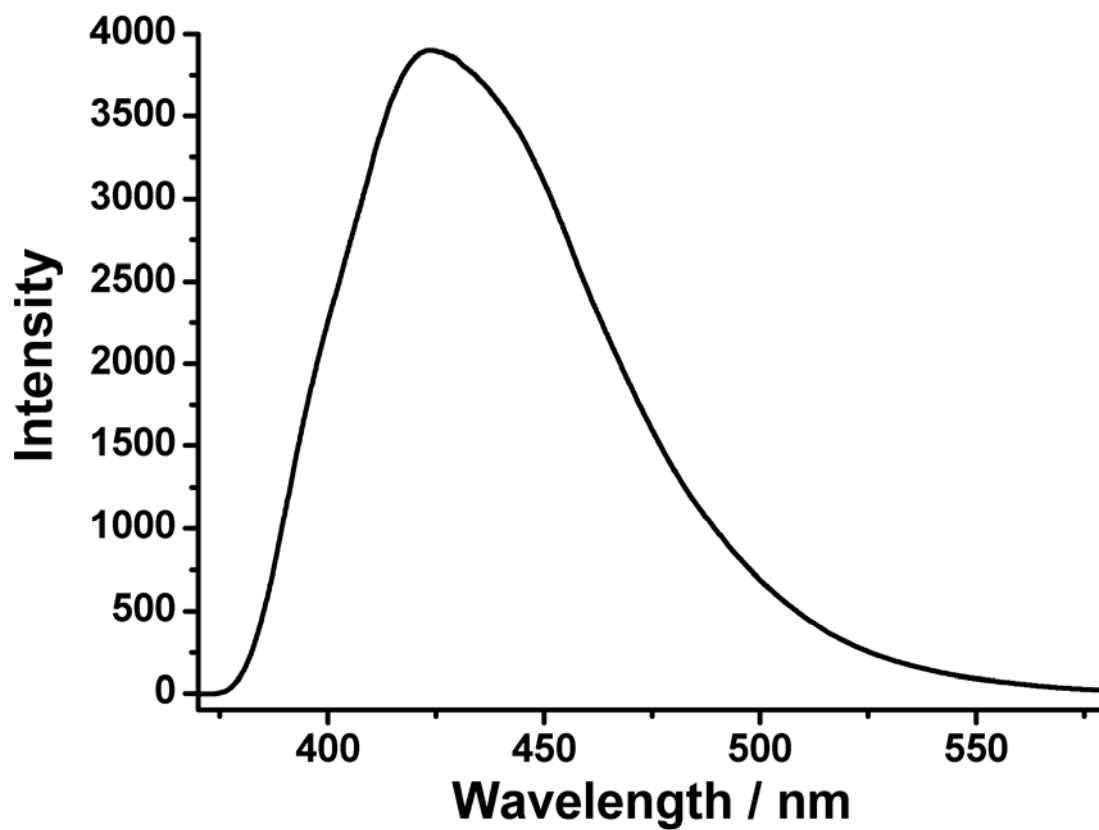


Figure S12. Phosphorescence spectrum of **BSA•Gd** in methanol–ethanol mixture (V : V = 1 : 1) at 77K.

6. Potentiometric titration of H₃BSA.

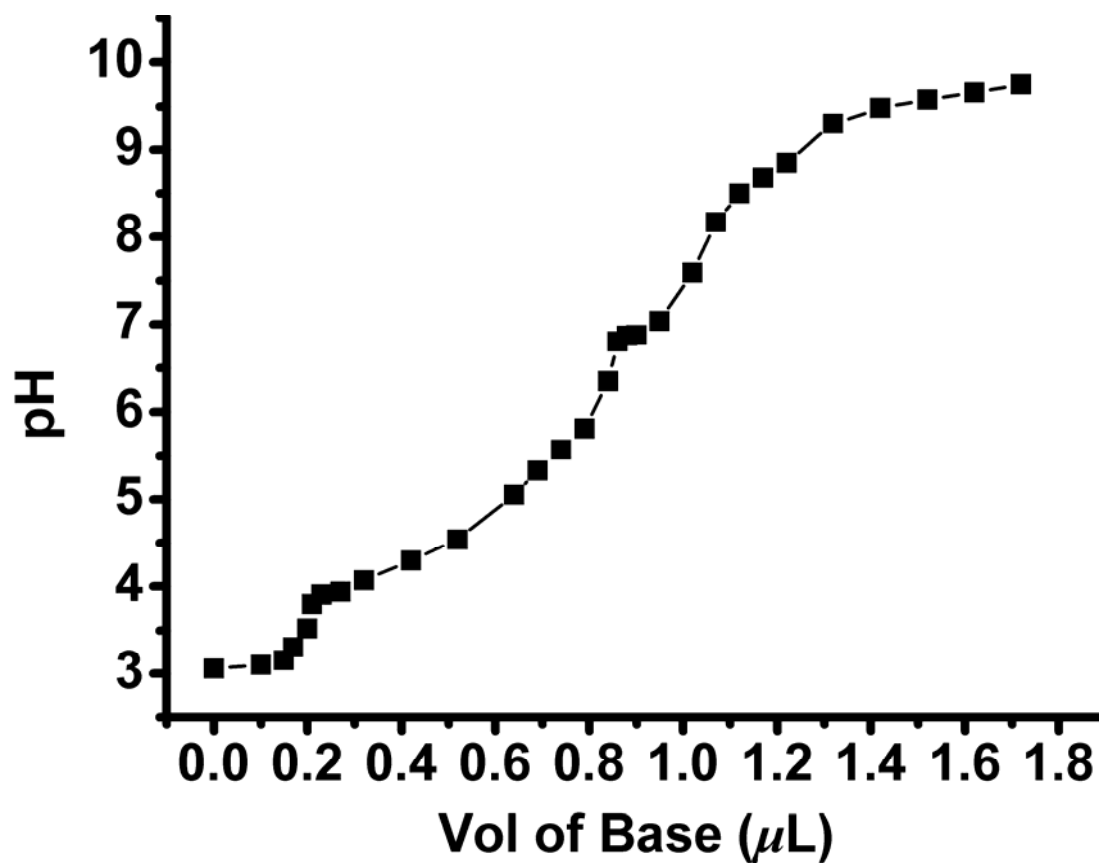


Figure S13. Titration plot of H₃BSA in water (1% DMSO, v/v) solution. [H₃BSA] = 1.0×10^{-4} M, [H⁺] = 0.01 M (HCl), [NaOH] = 0.01 M, *I* = 0.1 M (NaCl).

7. ESI-MS plot and the fluorescent spectrum of BSA•Tb at pH 2.0 in solution.

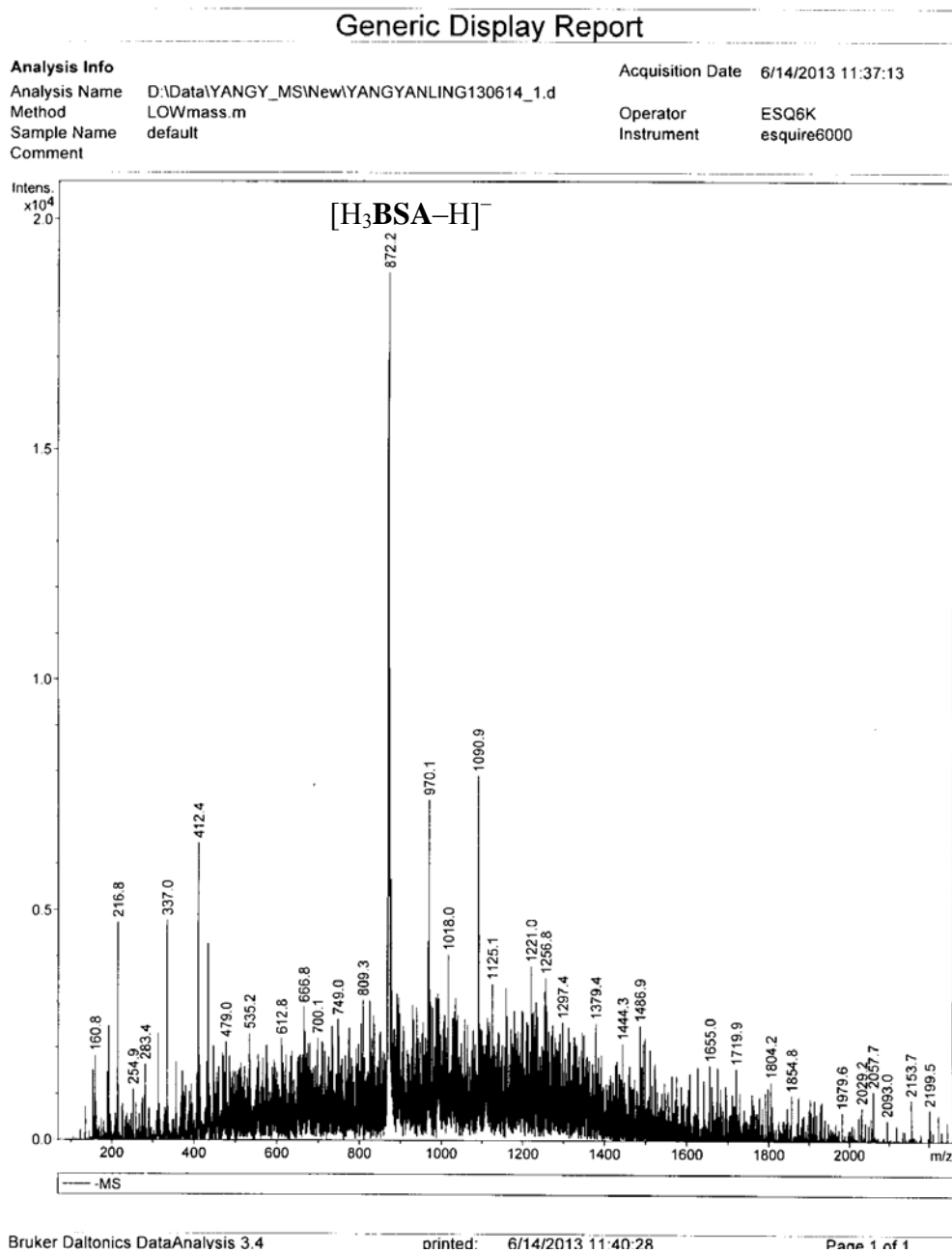


Figure S14. ESI mass spectrum of BSA•Tb at pH 2.0 in solution.

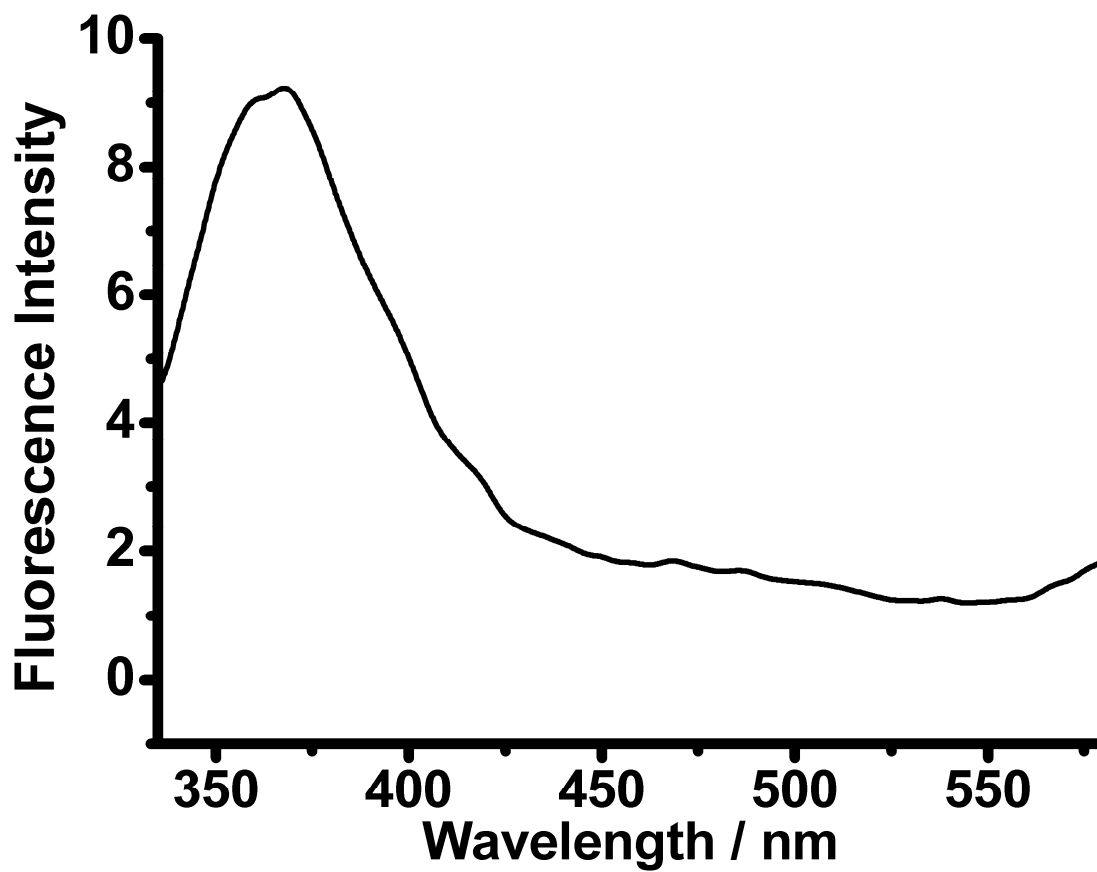


Figure S15. The fluorescent spectrum of **BSA•Tb** at pH 2.0 in Tris-buffer (1% DMSO, v/v) solution.

8. ESI-MS plot and the fluorescent spectrum of BSA•Tb at pH 9.0 in solution.

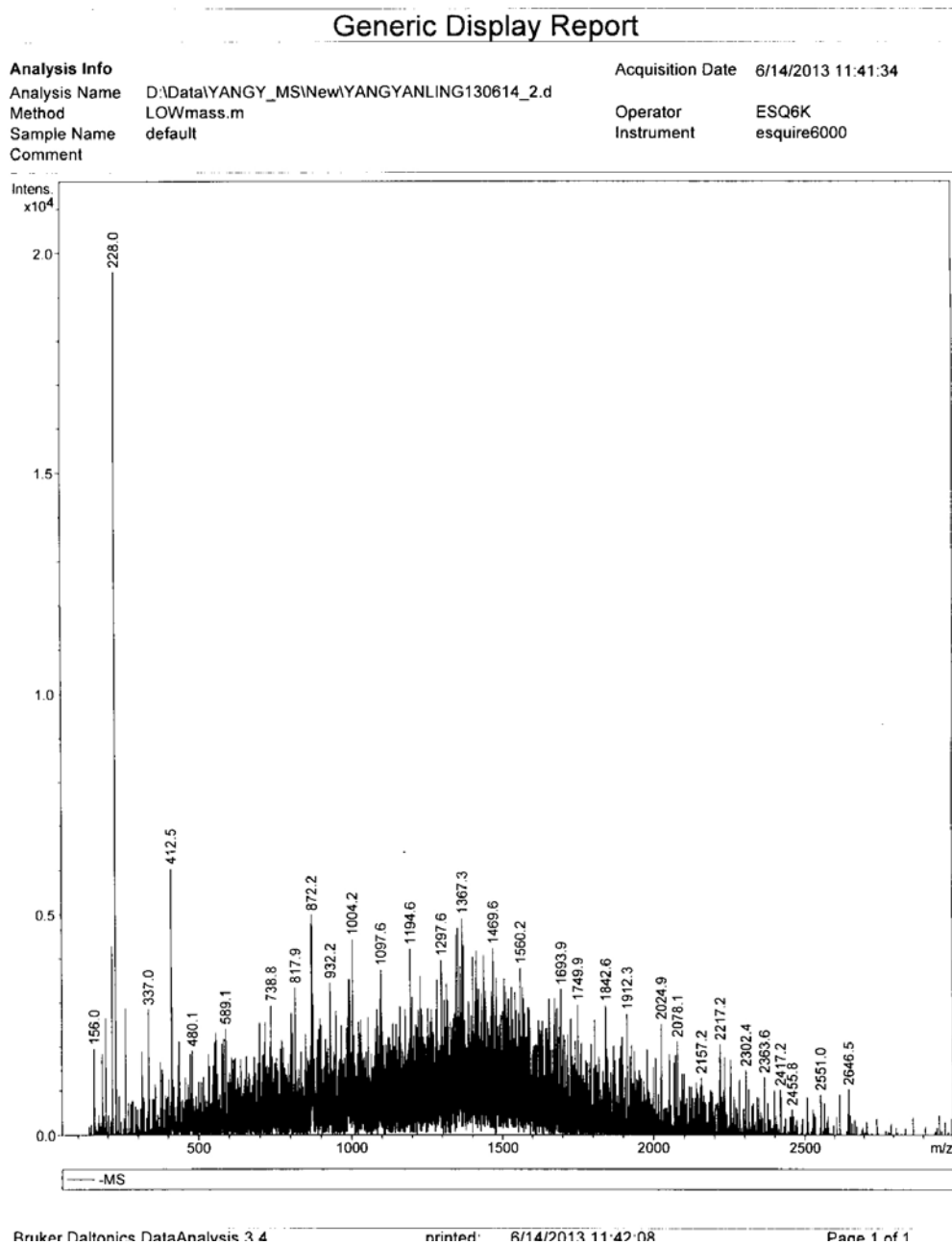


Figure S16. ESI mass spectrum of BSA•Tb at pH 9.0 in solution.

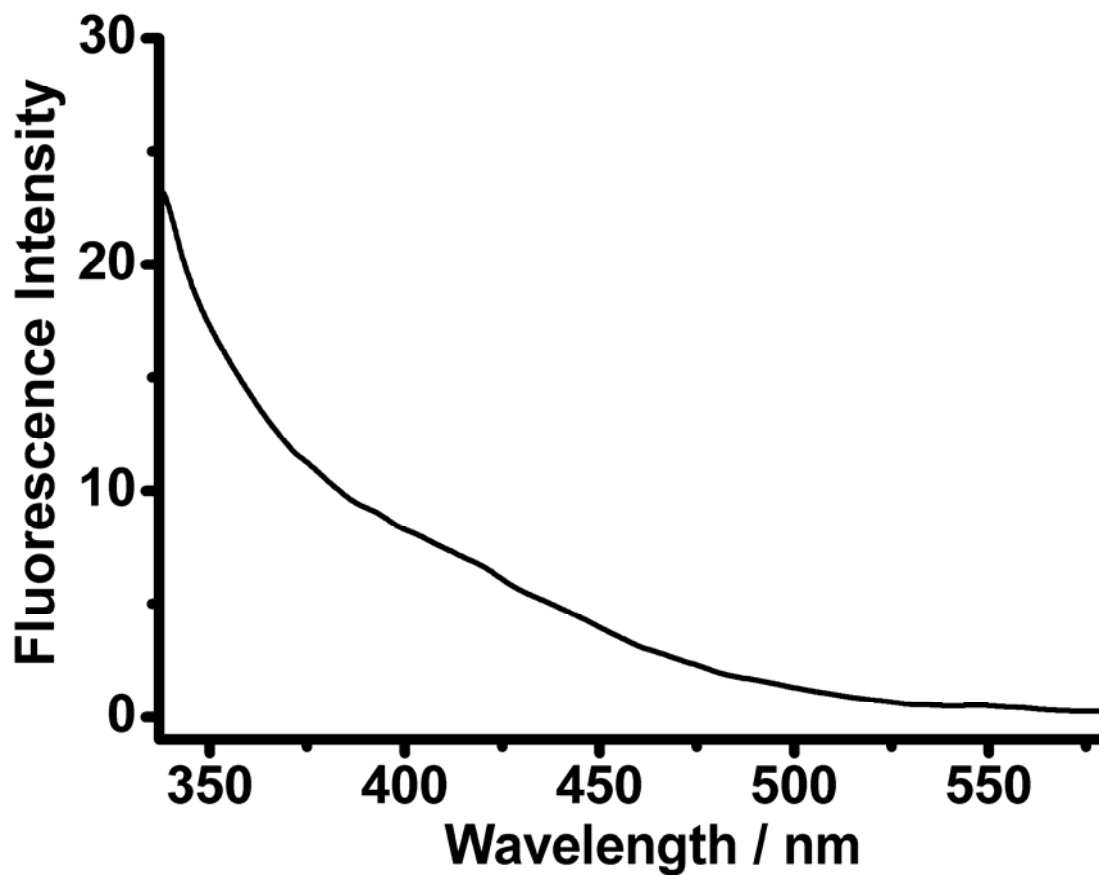


Figure S17. The fluorescent spectrum of **BSA•Tb** at pH 9.0 in Tris-buffer (1% DMSO, v/v) solution.

9. The pH dependence of the fluorescence intensity change of BSA•Eu.

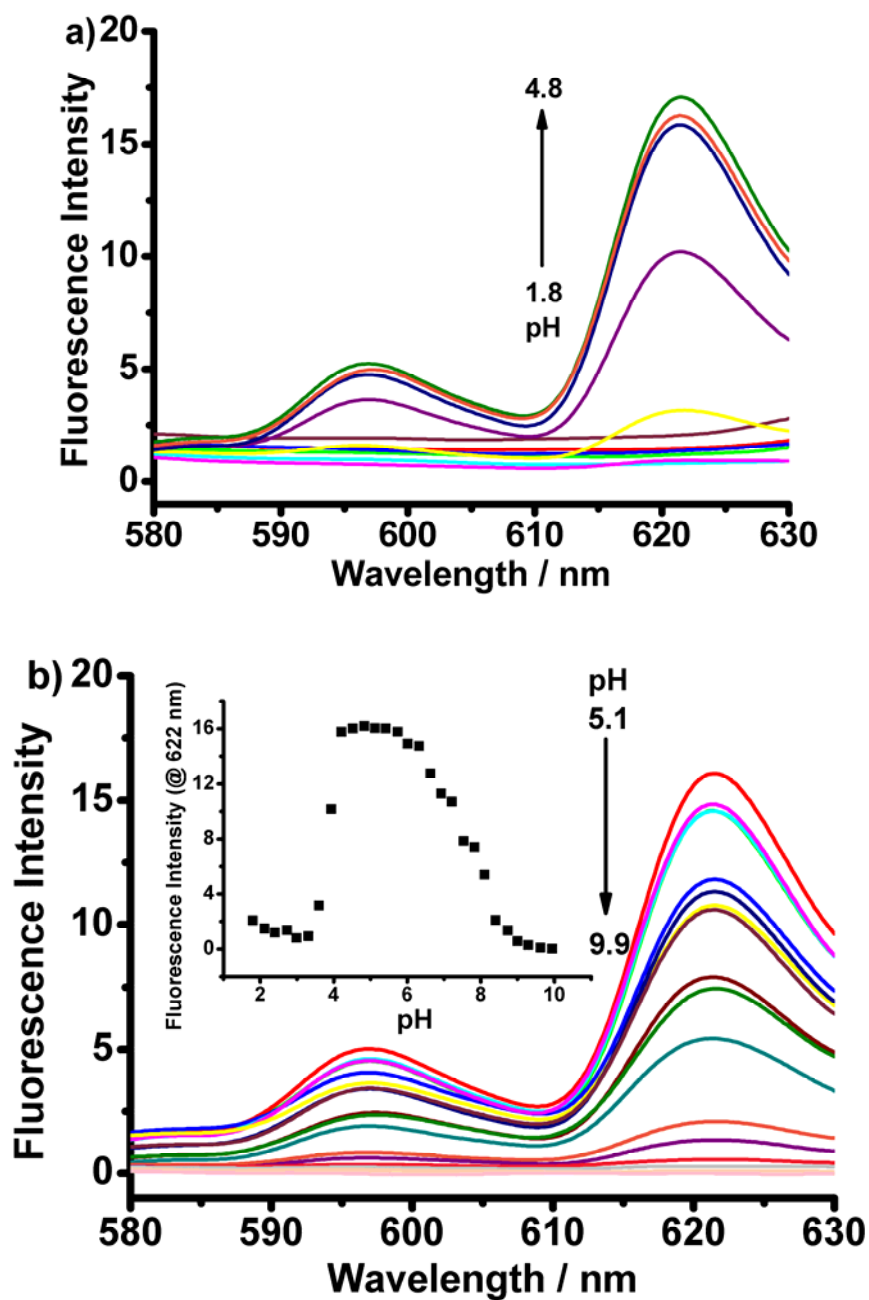


Figure S18. Fluorescent spectra of **BSA•Eu** (40.0 μM) in various pH values. (a) pH: 1.8, 2.1, 2.4, 2.7, 2.9, 3.0, 3.3, 3.6, 3.9, 4.2, 4.5, 4.8. (b) pH: 5.1, 5.4, 5.7, 6.0, 6.3, 6.6, 6.9, 7.2, 7.5, 7.8, 8.1, 8.4, 8.7, 9.0, 9.3, 9.6, 9.9. Inset: Fluorescence response of **BSA•Eu** to pH variation at 622 nm in Tris-buffer.

10. Fluorescence responses of BSA•Tb with Na⁺, K⁺, and Ca²⁺ ions in different pH values.

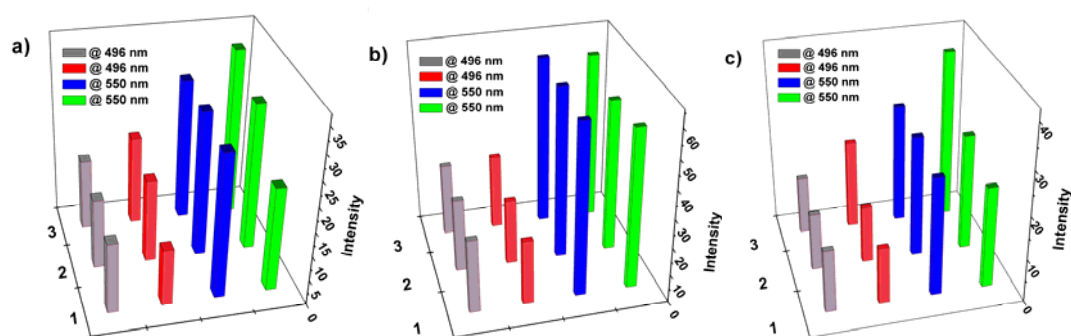


Figure S19. Fluorescence responses of **BSA•Tb** (20.0 μM) with Na⁺, K⁺, and Ca²⁺ ions in different pH values. a) pH: 5.0, b) pH: 6.5, c) pH: 7.4. The gray and blue bars represent the fluorescence emission of **BSA•Tb** in Tris-buffer (1% DMSO, v/v) solution at 496 and 550 nm, respectively. The red and green bars represent the fluorescence emission of **BSA•Tb** with addition of Na⁺ (150.0 mM), K⁺ (4.0 mM), and Ca²⁺ (1.0 mM) in Tris-buffer (1% DMSO, v/v) solution at 496 and 550 nm, respectively. From 1 to 3: Na⁺, K⁺, Ca²⁺.

11. Fluorescence responses of BSA•Tb with Cu^{2+} , Hg^{2+} , Fe^{2+} , and Fe^{3+} ions in different pH values.

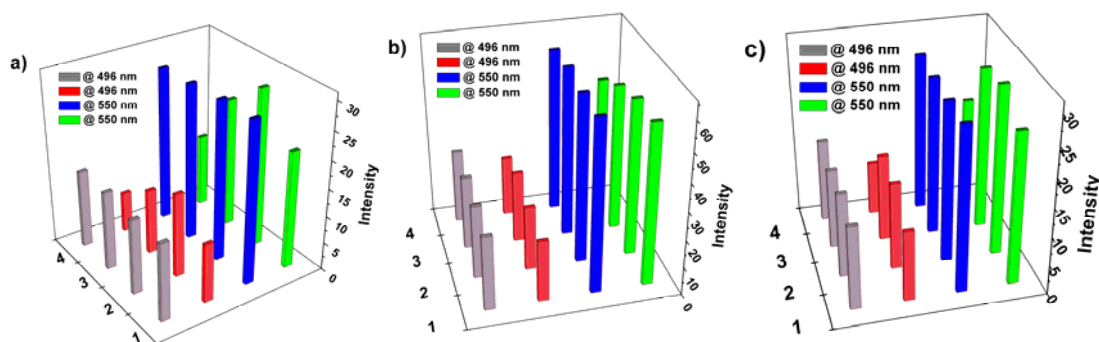


Figure S20. Fluorescence responses of **BSA•Tb** ($20.0 \mu\text{M}$) with Cu^{2+} , Hg^{2+} , Fe^{2+} , and Fe^{3+} ions in different pH values. a) pH: 5.0, b) pH: 6.5, c) pH: 7.4. The gray and blue bars represent the fluorescence emission of **BSA•Tb** in Tris-buffer (1% DMSO, v/v) solution at 496 and 550 nm, respectively. The red and green bars represent the fluorescence emission of **BSA•Tb** with addition 1.0 equiv of Cu^{2+} , Hg^{2+} , Fe^{2+} , and Fe^{3+} in Tris-buffer (1% DMSO, v/v) solution at 496 and 550 nm, respectively. From 1 to 4: Cu^{2+} , Hg^{2+} , Fe^{2+} , Fe^{3+} .

12. ORTEP plots of BSA•Eu and BSA•Gd.

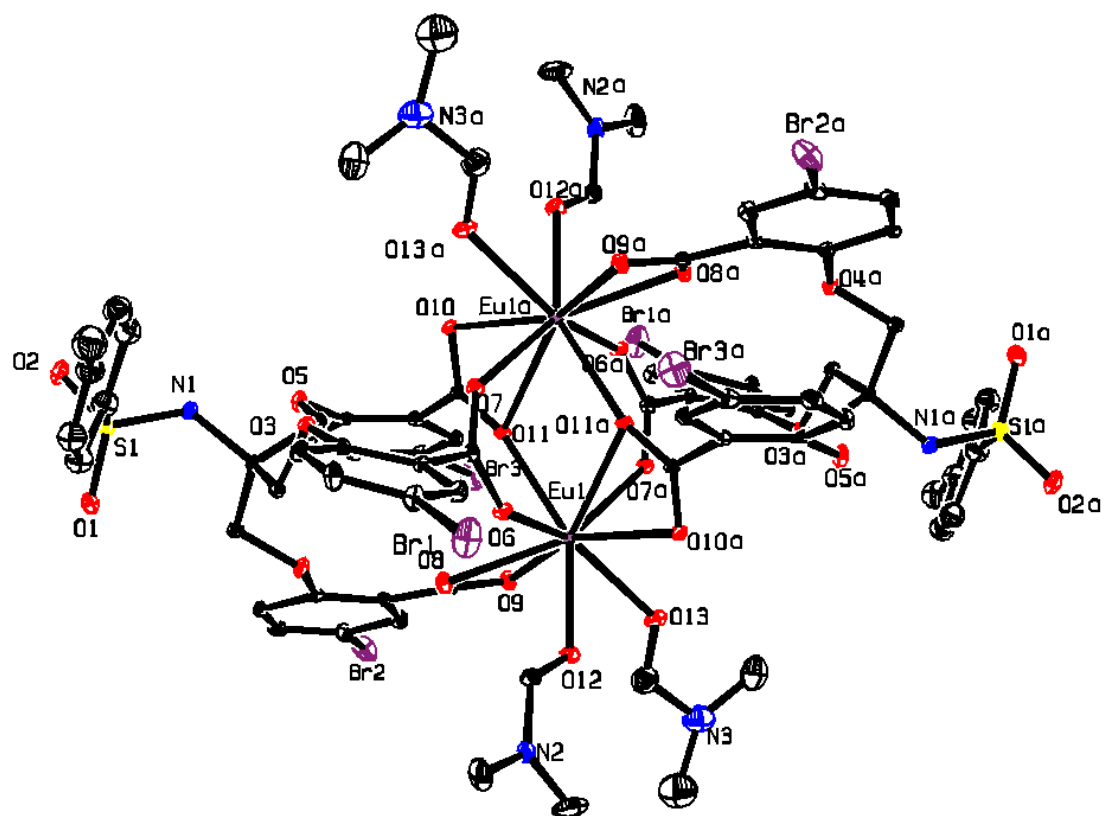


Figure S21. ORTEP plot of complex **BSA•Eu** with thermal ellipsoids at 30% probability (All hydrogen atoms are omitted for clarity). Symmetry operations: $a = 1 - x, -y, 2 - z$.

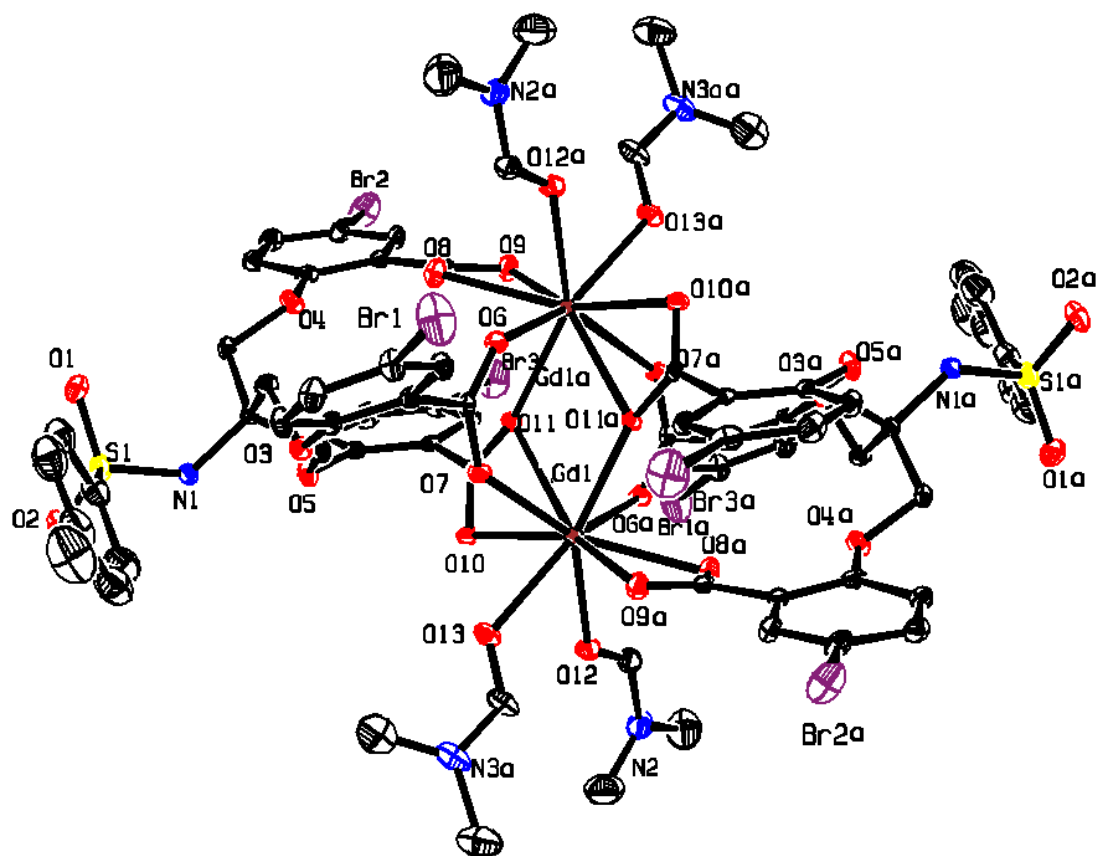


Figure S22. ORTEP plot of complex **BSA•Gd** with thermal ellipsoids at 30% probability (All hydrogen atoms are omitted for clarity). Symmetry operations: a = 1 - x, 1 - y, 1 - z.

13. Crystal data and structure refinement parameters for BSA•Eu, BSA•Gd and BSA•Tb.

Table S1 Crystal data and structure refinement parameters for **BSA•Eu**, **BSA•Gd** and **BSA•Tb**.

Compound	BSA•Eu	BSA•Gd	BSA•Tb
Empirical formula	C ₇₆ H ₇₄ Br ₆ Eu ₂ N ₆ O ₂₆	C ₇₆ H ₇₄ Br ₆ Gd ₂ N ₆ O ₂₆	C ₇₆ H ₇₄ Br ₆ Tb ₂ N ₆ O ₂₆
Temperature/K	296(2)	296(2)	296(2)
<i>M</i>	2334.90	2345.46	2348.82
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	12.839(4)	12.838(2)	12.818(2)
<i>b</i> /Å	12.860(4)	12.867(2)	12.868(2)
<i>c</i> /Å	16.021(5)	16.039(3)	16.038(3)
<i>a</i> /°	76.149(4)	76.149(2)	76.169(2)
<i>β</i> /°	87.883(4)	87.850(2)	87.766(2)
<i>γ</i> /°	88.339(4)	88.362(2)	88.385(2)
<i>V</i> /Å ³	2566.0(14)	2570.0(7)	2566.1(7)
<i>Z</i>	1	1	1
<i>D_c</i> /kg m ⁻³	1.511	1.515	1.520
<i>μ</i> /mm ⁻¹	3.653	3.718	3.809
<i>F</i> (000)	1148	1150	1152
Crystal size/mm	0.29 × 0.27 × 0.22	0.30 × 0.25 × 0.20	0.30 × 0.26 × 0.22
<i>θ</i> Range for data collection/°	2.25-20.22	2.30-21.82	2.26-22.66
Index ranges, <i>hkl</i>	-15 ≤ <i>h</i> ≤ 15, -14 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 19	-15 ≤ <i>h</i> ≤ 15, -14 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 19	-15 ≤ <i>h</i> ≤ 14, -15 ≤ <i>k</i> ≤ 15, -19 ≤ <i>l</i> ≤ 19
Reflections collected/unique	18846/9169	17141/9098	18184/9034
Data/restraints/params	9169/219/525	9098/816/575	9034/276/537
Goodness-of-fit on <i>F</i> ²	0.932	0.903	0.858
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0623, <i>wR</i> 2 = 0.1417	<i>R</i> 1 = 0.0443, <i>wR</i> 2 = 0.0846	<i>R</i> 1 = 0.0468, <i>wR</i> 2 = 0.1280
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1028, <i>wR</i> 2 = 0.1567	<i>R</i> 1 = 0.0688, <i>wR</i> 2 = 0.0907	<i>R</i> 1 = 0.0674, <i>wR</i> 2 = 0.1380

14. ESI-MS spectrum of H₃BSA with Tb(III) in Tris-buffer solution.

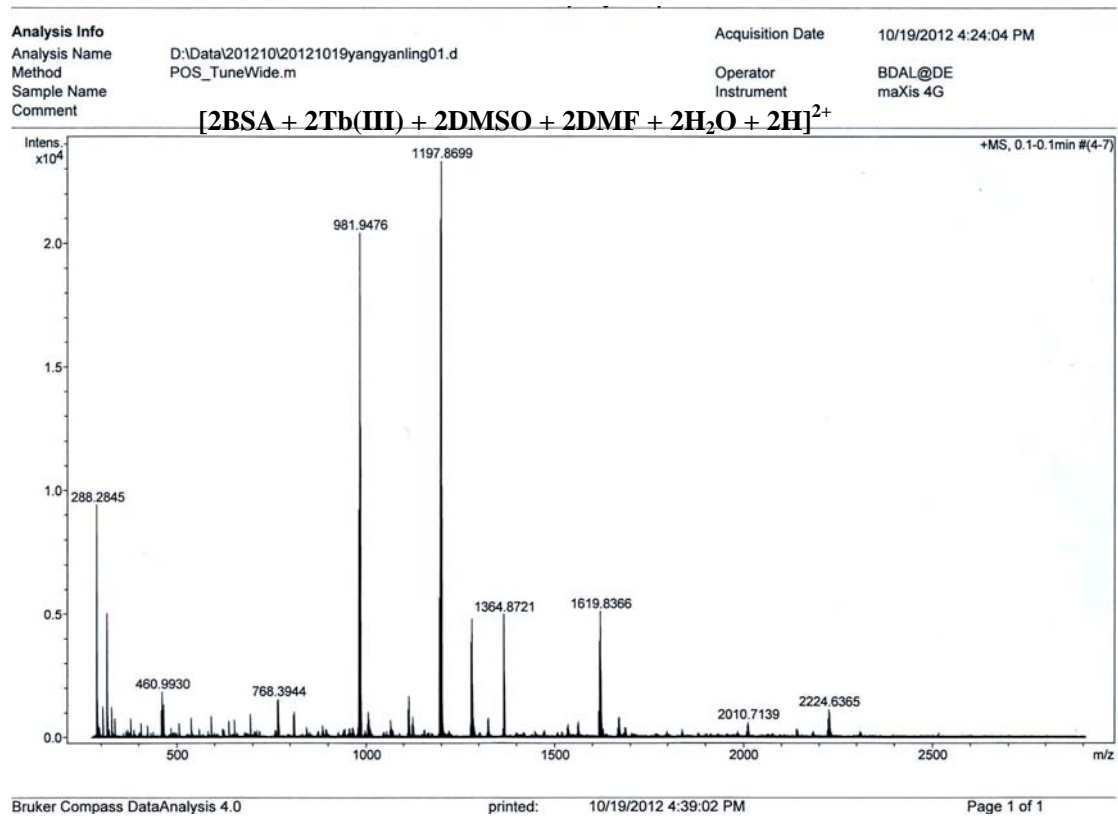


Figure S23. ESI-MS spectrum of H₃BSA with Tb³⁺ in Tris-buffer (1% DMSO, v/v) solution.

15. The supramolecular structure of BSA•Tb.

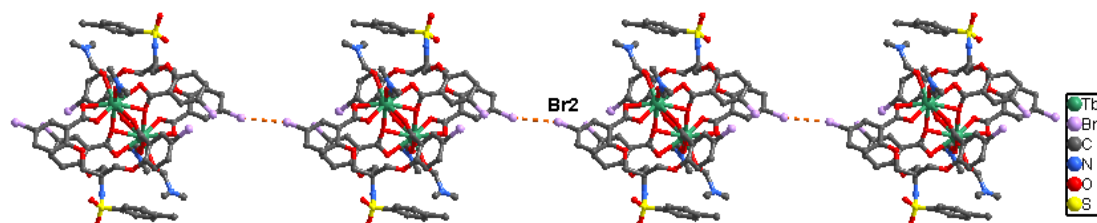


Figure S24. The 1D chain of **BSA•Tb** formed by Br...Br interactions indicated with dashed orange lines (Some atoms are omitted for clarity).

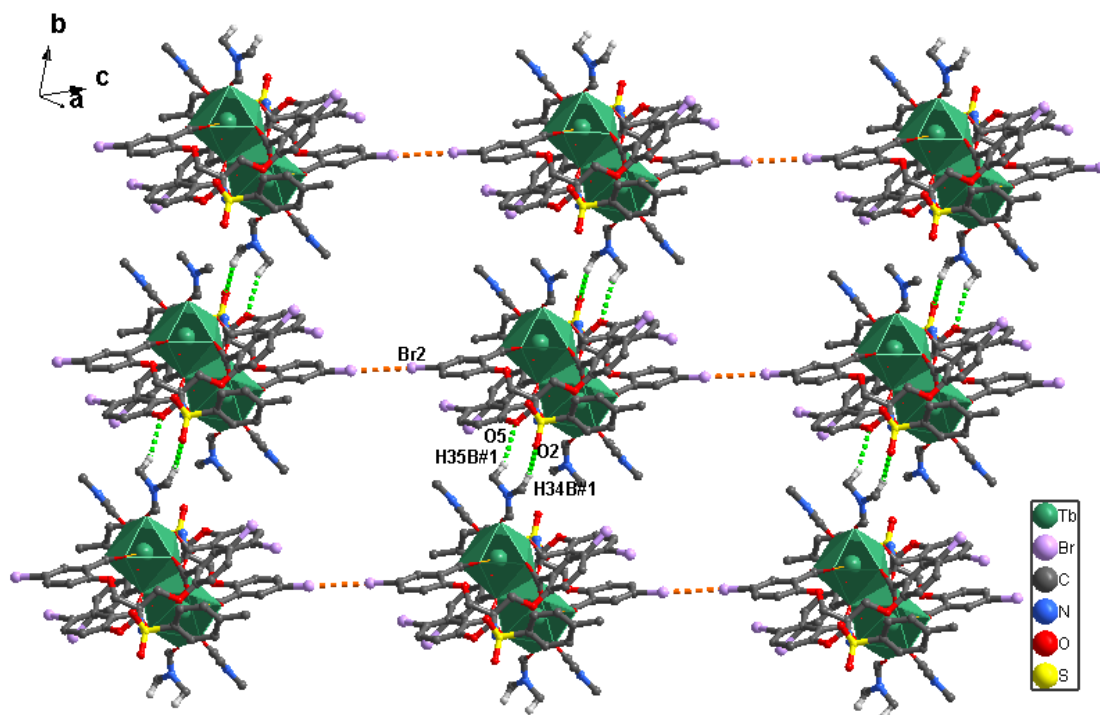


Figure S25. The 2D supramolecular sheet of **BSA•Tb** constructed by C-H...O hydrogen bonding indicated with dashed green lines (Some atoms are omitted for clarity). Symmetry operations: #1 = x, -1 + y, z.

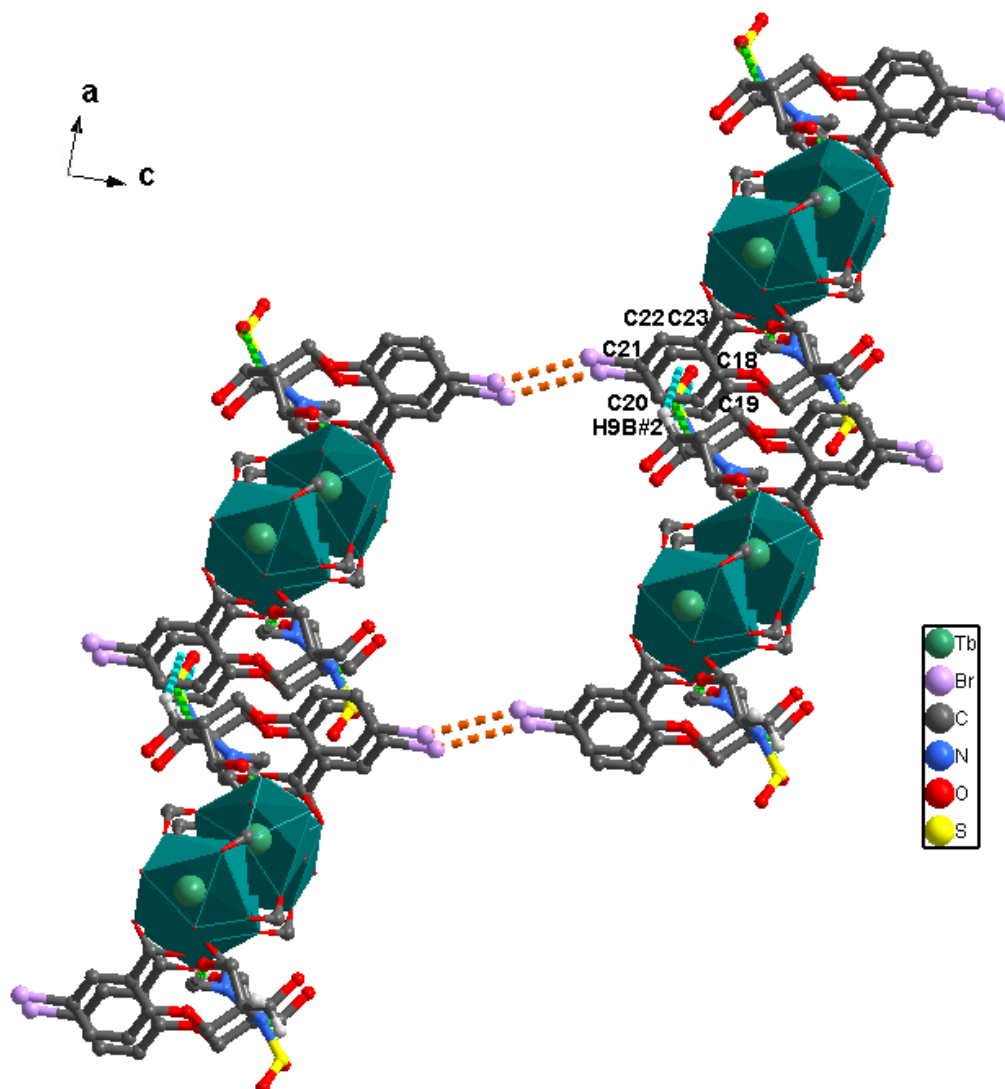


Figure S26. The 3D supramolecular chains of **BSA•Tb** constructed by the intermolecular T-shaped C-H... π interactions which are indicated with dashed turquoise lines (Some atoms are omitted for clarity). Symmetry operations: #2 = $1 - x$, $1 - y$, $1 - z$.