

## **Electronic Supplementary Information (ESI)**

### **A turn-on fluorogenic Zn (II) chemoprobe based on a terpyridine derivative with aggregation-induced emission (AIE) effects through nanofiber aggregation into spherical aggregates**

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## Experimental Section

**Characterization.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker DRX 300 apparatus. Mass spectra were obtained by a JEOL JMS-700 mass spectrometer. The optical absorption spectra of the samples were obtained at 298K using a UV-Vis spectrophotometer (Thermo Evolution 600). All fluorescence spectra were recorded in RF-5301PC spectrophotometer. Elemental analyses were performed with a Perkin Elmer 2400 series II.

**TEM observations.** For transmission electron microscopy (TEM), the samples were placed on a carbon-coated copper grid (400 mesh) and then removed after one minute, leaving some small patches of sample on the grid. This was examined using a JEOL JEM-2010 transmission electron microscope operating at 200 kV with an acceleration voltage of 100 kV and a 16 mm working distance.

**SEM observations.** For Scanning electron micrographs of the samples were taken with a field emission scanning electron microscope (FE-SEM, Philips XL30 S FEG). The accelerating voltage of SEM was 5–15 kV and the emission current was 10  $\mu\text{A}$ .

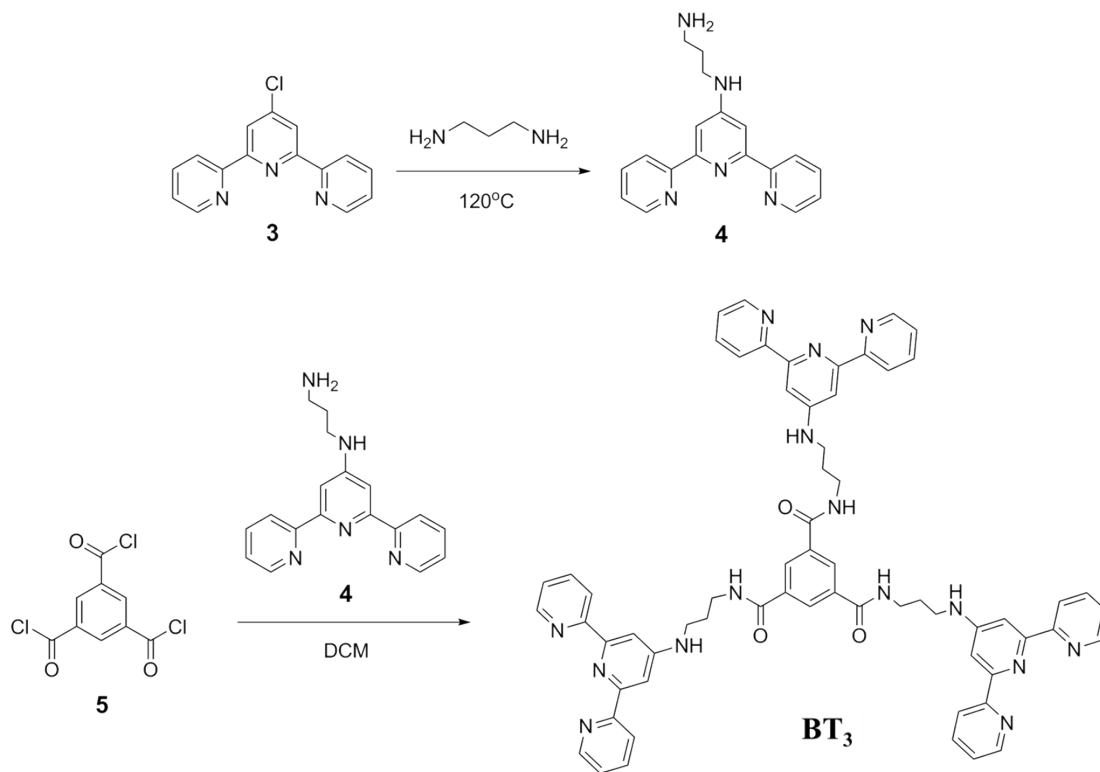
**Preparation of aggregated  $\text{BT}_3$ .** Stock solutions of the  $\text{BT}_3$  in DMSO with a concentration of 100  $\mu\text{M}$  were prepared. Aliquots (1.0 mL) of the stock solutions were transferred to 10 mL volumetric flasks. After adding appropriate amounts of DMSO, water was added dropwise under vigorous stirring to furnish 10  $\mu\text{M}$  solutions with defined fractions of water (fw = 0–99 vol %). Spectral measurements of the resultant solutions or aggregate suspensions were performed immediately.

**Preparation of aggregated  $\text{BT}_3$  with metal ions.** Stock solutions of the  $\text{BT}_3$  in DMSO was diluted to 10  $\mu\text{M}$  using water (fw = 99 vol %), followed by the addition of an aliquot of different metal ions. The final concentration of the metal ions was 15  $\mu\text{M}$  unless specified. The solutions were mixed by Vortex and stood for 10 min prior to spectral measurement.

**Detection of  $\text{Zn}^{2+}$  concentration in urine.** Human urine samples were collected from healthy adult. 2 mL urine sample was transferred to 10 mL volumetric flasks. After  $\text{Zn}^{2+}$  was added as internal standard (0, 200, 400, 600, 800 and 1000  $\mu\text{M}$ ) following by diluting to scale with water. Then 100  $\mu\text{M}$  of the spiked  $\text{Zn}^{2+}$  in urine was transferred into the 10 mL volumetric flasks containing  $\text{BT}_3$  (10  $\mu\text{M}$ ) in DMSO/water mixture (1:99 v/v). The final concentrations of the spiked  $\text{Zn}^{2+}$  were 0, 2, 4, 6, 8 and 10  $\mu\text{M}$ . The solutions were mixed by Vortex and stood for 10 min prior to spectral measurement.

**Preparation of compound 4:** 4'-Chloro-[2,2';6',2'']terpyridine (4'-chloroter-pyridine), (0.9 g, 3.36 mmol) was suspended in 1,3-diamino propane (6.5 mL). Upon heating a yellow solution was observed. The reaction mixture was then heated under reflux conditions (120  $^\circ\text{C}$ ) overnight. After cooling to room temperature,  $\text{H}_2\text{O}$  (50 mL) was added and a white precipitate was formed, which was filtered and further washed with  $\text{H}_2\text{O}$ . The solid was dissolved in dichloromethane and extracted twice with  $\text{H}_2\text{O}$ . The organic layers were combined and dried over  $\text{Na}_2\text{SO}_4$ , filtered and the solvent removed under reduced pressure to yield a white solid (0.8g, 78%). m.p. 147  $^\circ\text{C}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ) 8.67 (d, 2H,  $\text{CH}_6+6''$ ,  $J = 4.8$  Hz) 8.62 (d, 2H,  $\text{CH}_3+3''$ ,  $J = 7.8$  Hz) 7.83 (t, 2H,  $\text{CH}_4+4''$ ,  $J = 7.8, 7.8$  Hz) 7.68 (s, 2H,  $\text{CH}_3'+5'$ ), 7.31 (t, 2H,  $\text{CH}_5+5''$ ,  $J = 6.0, 6.3$  Hz), 5.12 (t, 1H, NH,  $J = 4.5, 5.0$ Hz), 3.48 (m, 2H,  $\text{NHCH}_2$ ), 2.92 (t, 2H,  $\text{CH}_2$ ,  $J = 6.6, 6.3$  Hz) 1.84 (m, 2H,  $\text{NH}_2\text{CH}_2$ ) 1.35 (bs, 2H,  $\text{NH}_2$ );  $^{13}\text{C-NMR}$  (125MHz,  $\text{CDCl}_3$ ) 156.89, 155.84, 155.49, 148.82, 136.66, 123.41, 121.32, 104.62, 41.68, 40.42, 32.33; IR(KBr,  $\text{cm}^{-1}$ ): 3353, 3245, 3126, 3051, 3012, 2932, 2852, 1618, 1572, 1564, 1515, 1464, 1456, 1447, 1407, 1355, 1339, 1314, 1296, 1225, 1113, 1091, 1069, 1040, 986, 924, 861, 798, 743, 697, 657; ESI-MS:  $m/z$  306.25  $[\text{M} + \text{H}]^+$ ; Calculated for  $\text{C}_{18}\text{H}_{19}\text{N}_5$   $[\text{M} + \text{H}]^+$  306.3734, Found 306.3719.

**Preparation of compound  $\text{BT}_3$ .** The ligand  $\text{BT}_3$  was prepared according to a literature procedure.<sup>1</sup> A solution of 4 (0.05 g, 0.164 mmol) in dichloromethane was allowed to cool in an acetone/ice bath for 15 minutes before adding 1,3,5-benzenetricarbonyl trichloride (0.014 g, 0.053 mmol). A white precipitate was observed and the reaction mixture was further stirred at room temperature overnight. The solid was then filtered and washed with dichloromethane to yield a beige solid (0.051 g, 90 %). m.p. 230  $^\circ\text{C}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{CD}_3\text{OD}$ ) 8.72 (s, 1H,  $\text{CH}_{\text{tpy}}$ ), 8.71 (s, 1H,  $\text{CH}_{\text{tpy}}$ ), 8.68 (s, 1H,  $\text{CH}_{\text{benzene}}$ ), 8.35 (s, 1H,  $\text{CH}_{\text{tpy}}$ ), 8.13-8.00 (3H,  $\text{CH}_{\text{tpy}}$ ), 7.62-7.46 (4H,  $\text{CH}_{\text{tpy}}$ ), 3.65 (m, 2H,  $\text{CH}_2$ ), 3.65 (m, 2H,  $\text{CH}_2$ ), 2.12 (m, 2H,  $\text{CH}_2$ );  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CD}_3\text{OD}$ ) 167.22, 160.36, 160.04, 149.99, 146.83, 145.90, 138.54, 138.25, 135.17, 131.91, 131.67, 131.17, 129.31, 126.85, 121.73, 121.73, 110.65, 106.05, 100.79, 41.30, 37.43, 28.21; IR(KBr,  $\text{cm}^{-1}$ ): 3245, 3094, 3058, 2942, 2871, 1637, 1589, 1527, 1464, 1443, 1352, 1297, 1270, 1238, 1159, 1124, 1090, 1034, 993, 908, 867, 785, 736; ESI-MS:  $m/z$  358.25  $[\text{M} + 3\text{H}]^{3+}/3$ , 536.92  $[\text{M} + 2\text{H}]^{2+}/2$ , 1072.58  $[\text{M} + \text{H}]^+$ ; Calculated for  $\text{C}_{63}\text{H}_{59}\text{N}_{15}\text{O}_3$  1073.4925, Found 1073.4930.



Scheme S1. Synthesis of terpyridine-based ligand BT<sub>3</sub>.

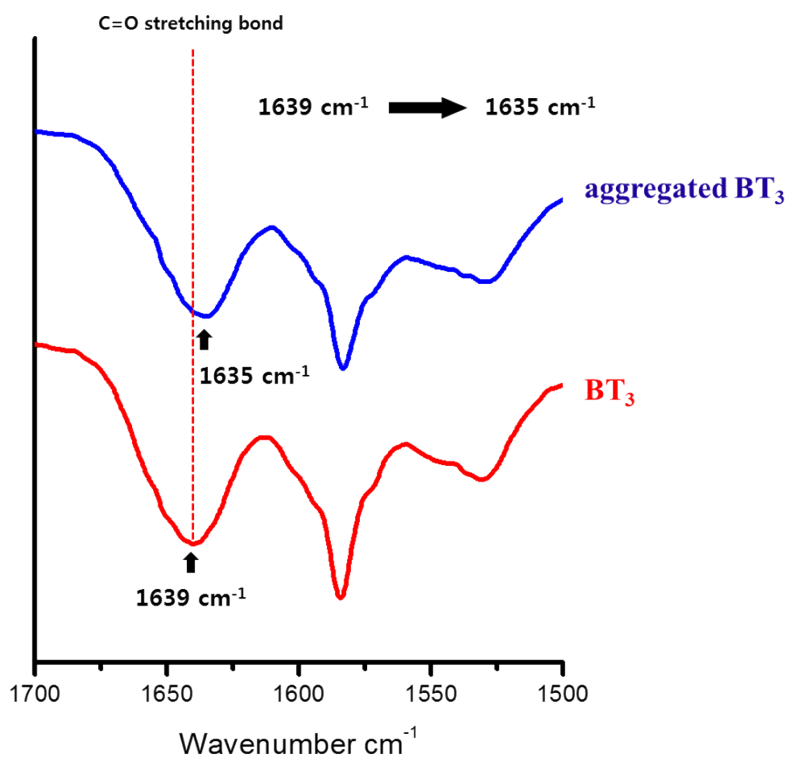
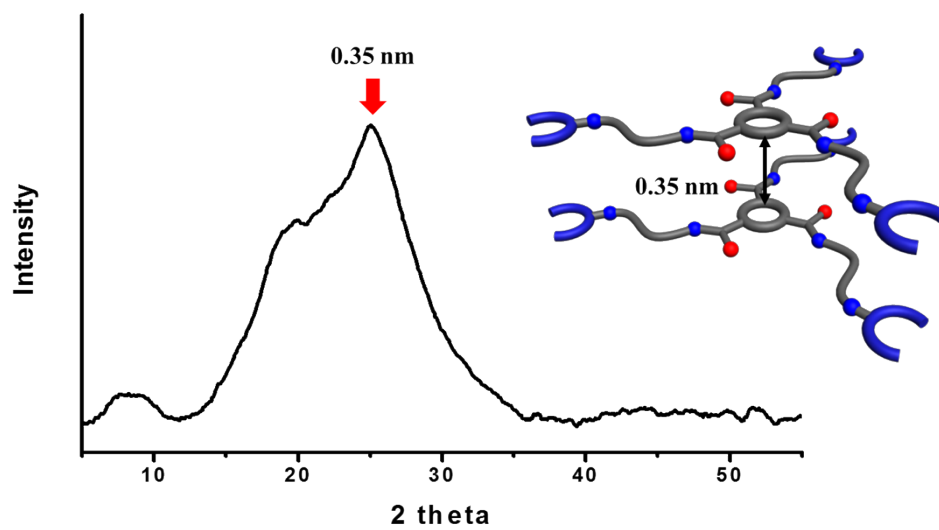
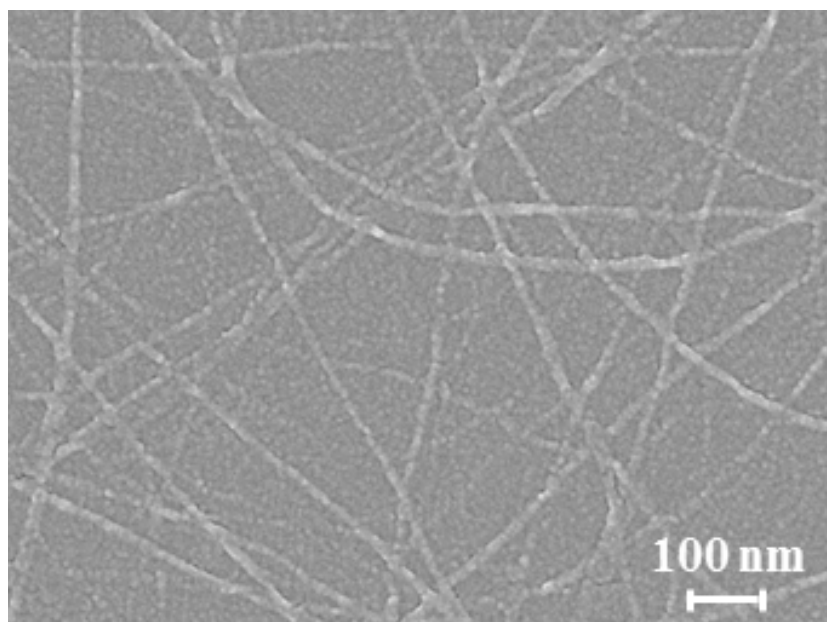


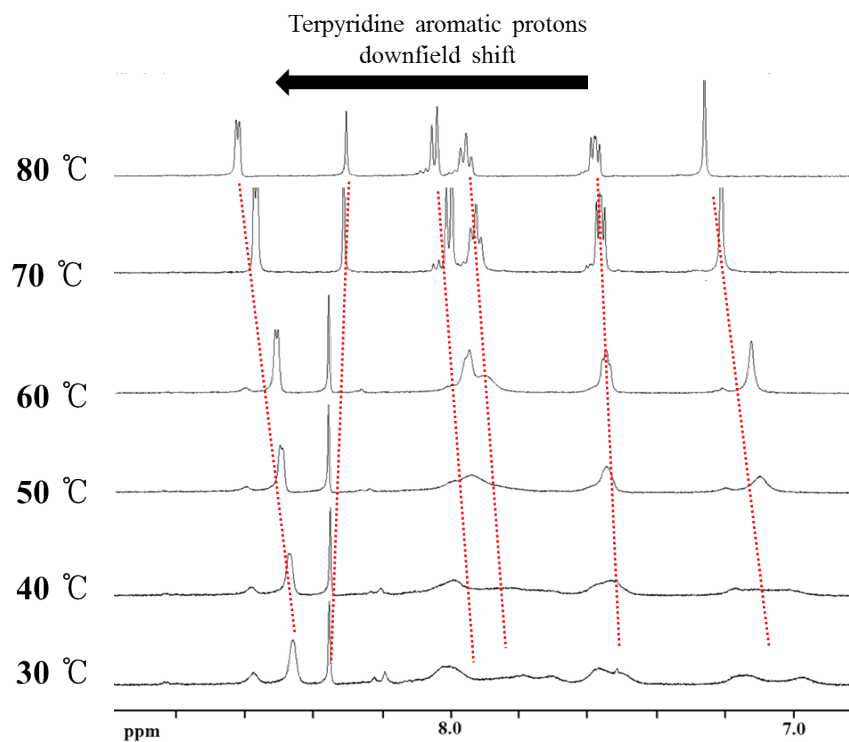
Fig. S1 IR spectra of BT<sub>3</sub> and after aggregated BT<sub>3</sub>.



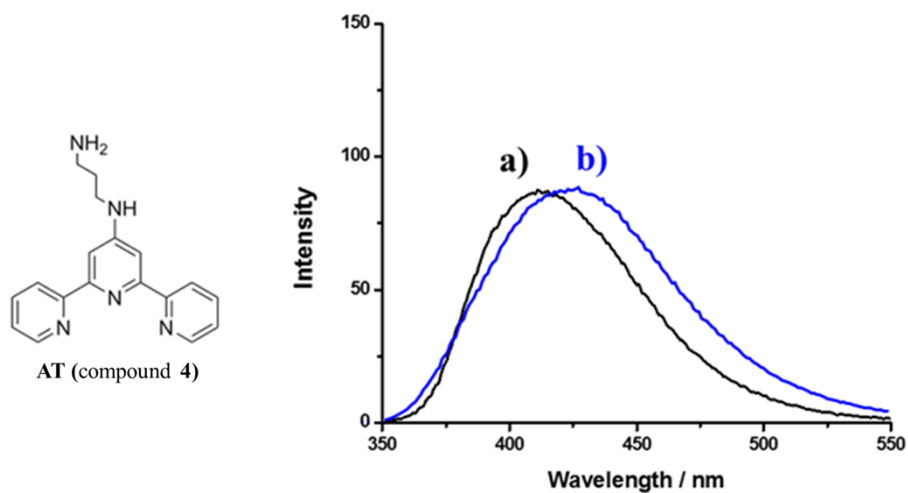
**Fig. S2** Powder X-ray diffraction analysis of aggregated BT<sub>3</sub>.



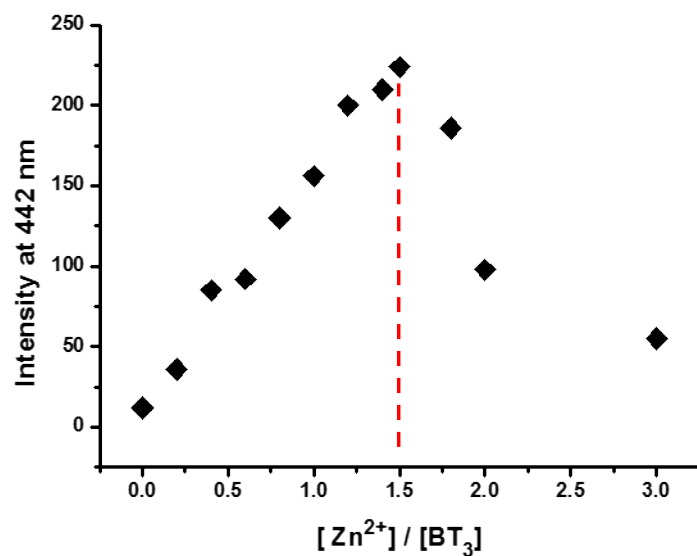
**Fig. S3** SEM image of BT<sub>3</sub> prepared in DMSO/water mixture (1:99 v/v).



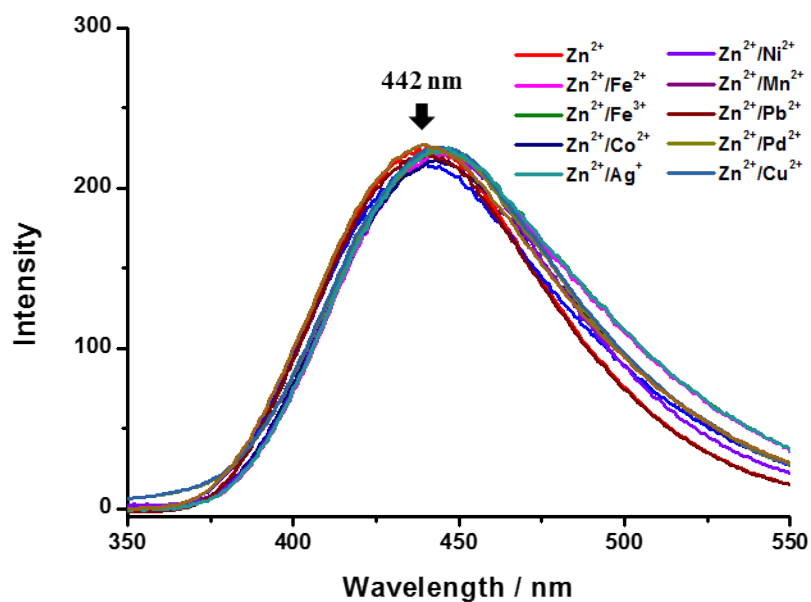
**Fig. S4** Variable temperature (VT)  $^1\text{H}$  NMR spectra of  $\text{BT}_3$  ( $10\ \mu\text{M}$ ) in DMSO/water mixtures as increasing temperature.



**Fig. S5** Fluorescence spectra of a) **AT** (compound: **4**,  $10\ \mu\text{M}$ ) and b) **AT** in the presence of  $\text{Zn}^{2+}$  ( $15\ \mu\text{M}$ ) in DMSO/water mixture (1/99 v/v).



**Fig. S6.** Fluorescence titration curve of **BT<sub>3</sub>** upon addition of **Zn<sup>2+</sup>**. Condition: **BT<sub>3</sub>**, 10  $\mu$ M; **Zn<sup>2+</sup>**, 0.1-3.0 x 10  $\mu$ M, plotted at 442 nm.



**Fig. S7.** Fluorescence spectra of **Zn<sup>2+</sup>**-bound **BT<sub>3</sub>** in DMSO/water mixture (1/99 v/v) in the presence other metal ions.

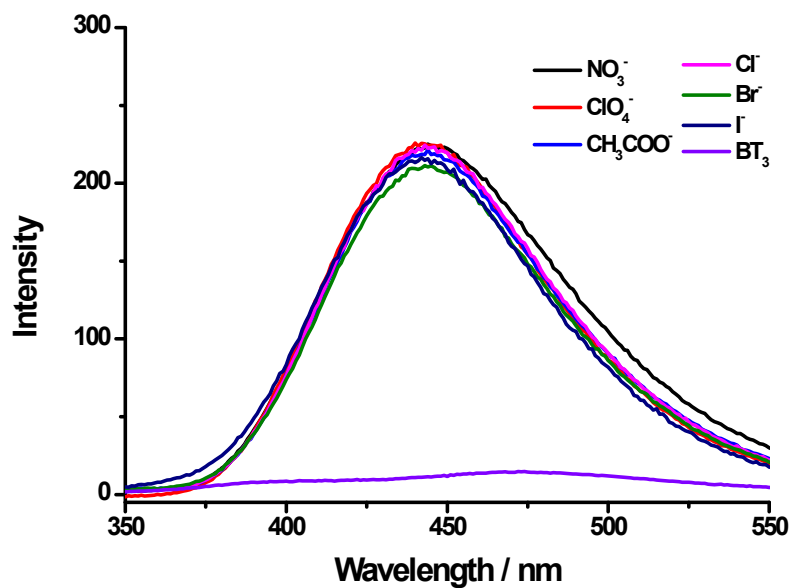


Fig. S8. Fluorescence spectra of Zn<sup>2+</sup>-bound BT<sub>3</sub> in DMSO/water mixture (1/99 v/v) with different anions.

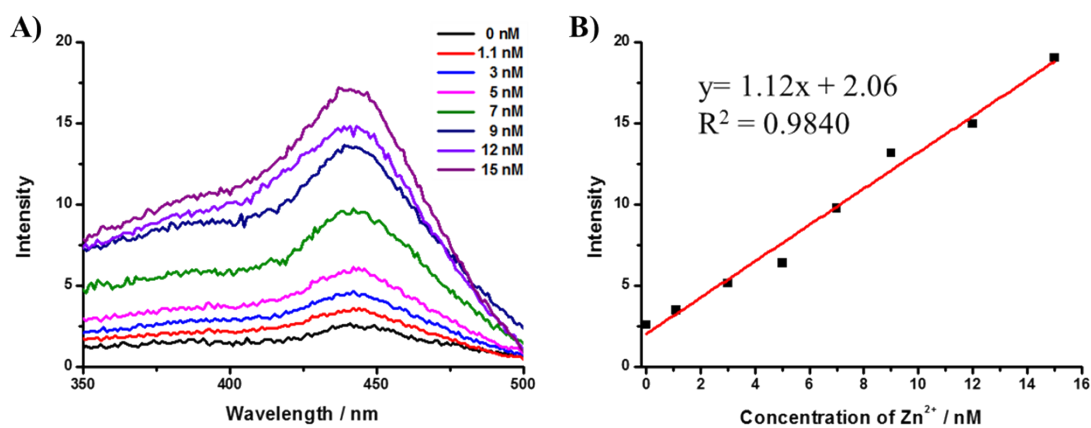
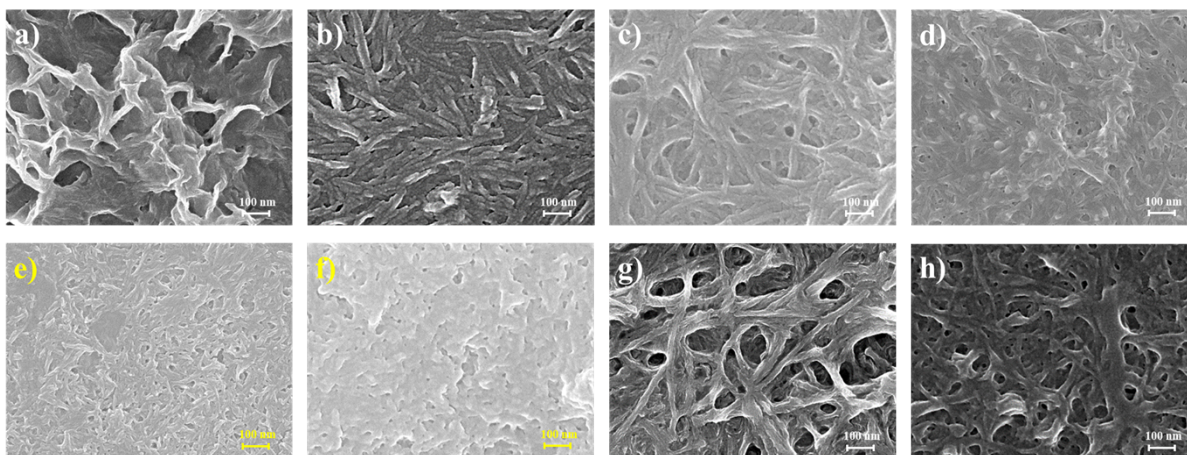
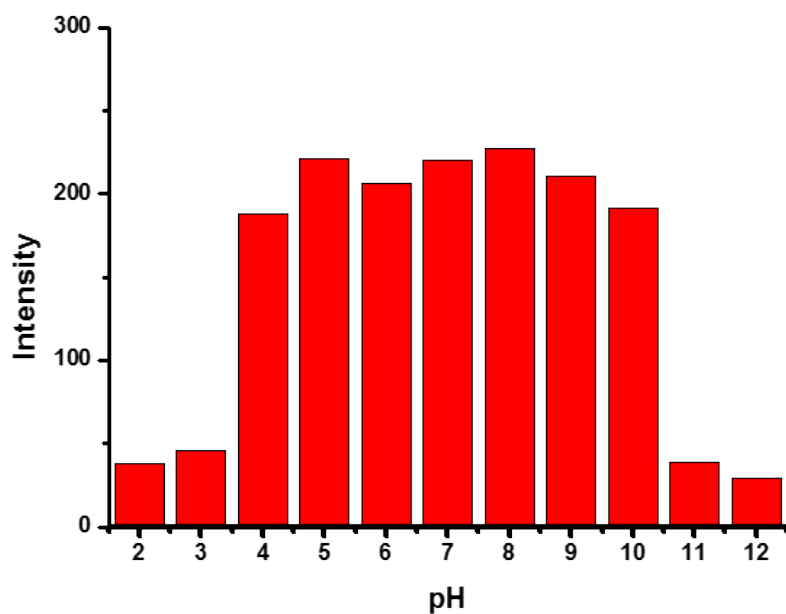


Fig. S9. A) Fluorescence spectra of BT<sub>3</sub> upon addition of Zn<sup>2+</sup> (1.1-15 nM) in DMSO/water mixture (1/99 v/v). B) Plot of fluorescence intensity of BT<sub>3</sub> with Zn<sup>2+</sup> (1.1-15 nM) at 442 nm.

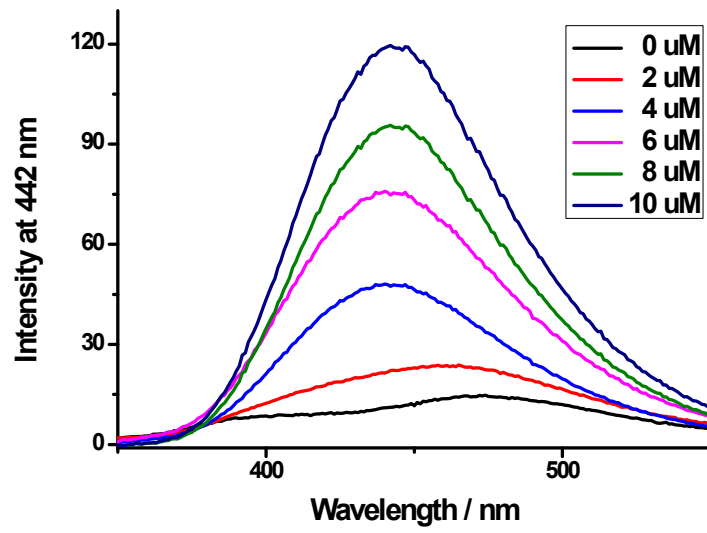


**Fig. S10.** SEM images of  $\text{BT}_3$  in presence of various metal ions in DMSO/water mixture (1:99 v/v); a)  $\text{Co}^{2+}$ , b)  $\text{Ni}^{2+}$ , c)  $\text{Mn}^{2+}$ , d)  $\text{Pb}^{2+}$ , e)  $\text{Cu}^{2+}$ , f)  $\text{Fe}^{2+}$ , g)  $\text{Fe}^{3+}$  and h)  $\text{Ag}^+$ .

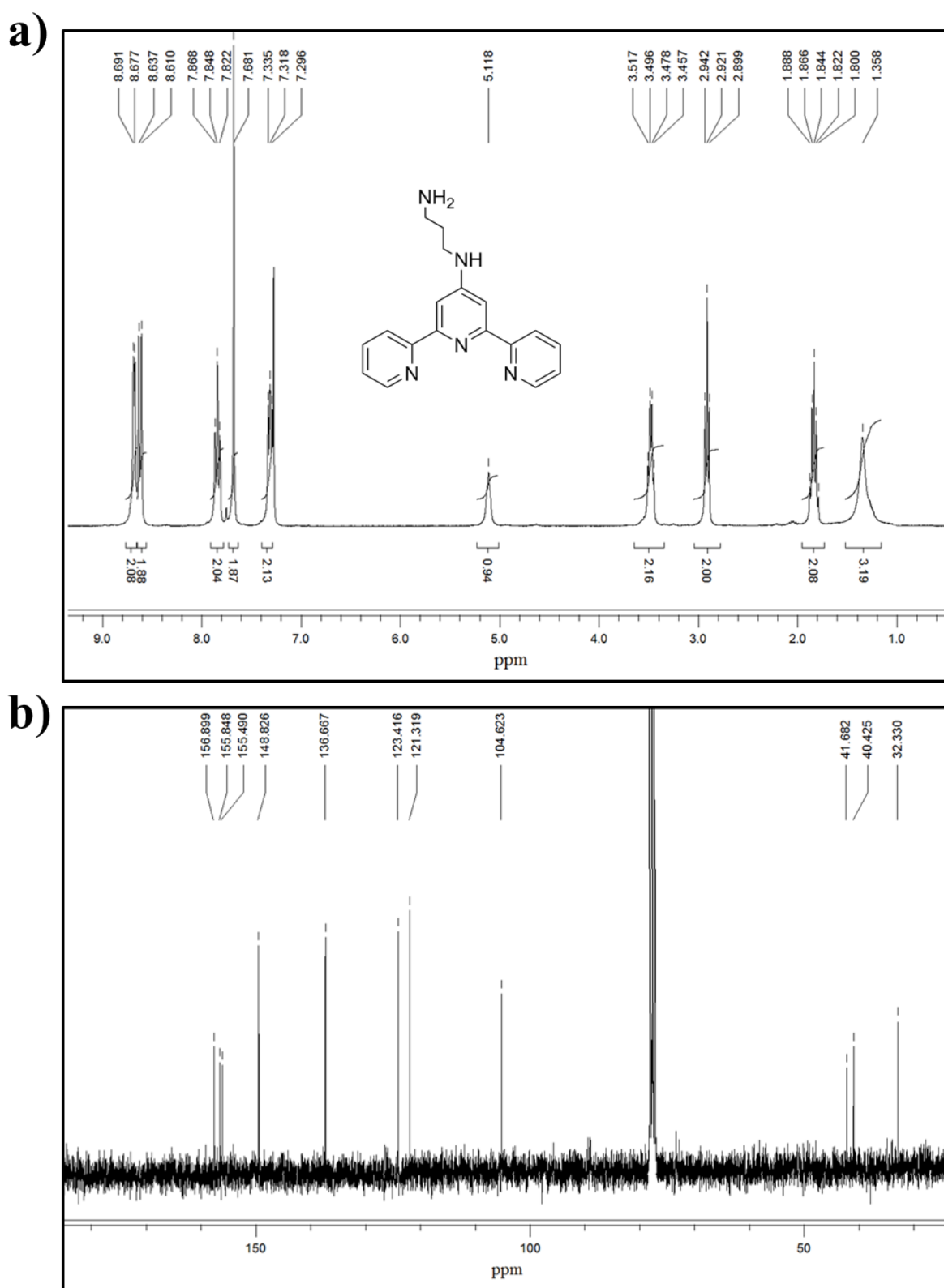


**Fig. S11.** A) Fluorescence intensity of  $\text{BT}_3$  (10  $\mu\text{M}$ ) in the presence of  $\text{Zn}^{2+}$  (15  $\mu\text{M}$ ) in DMSO/water mixture (1/99 v/v) at different pH values.

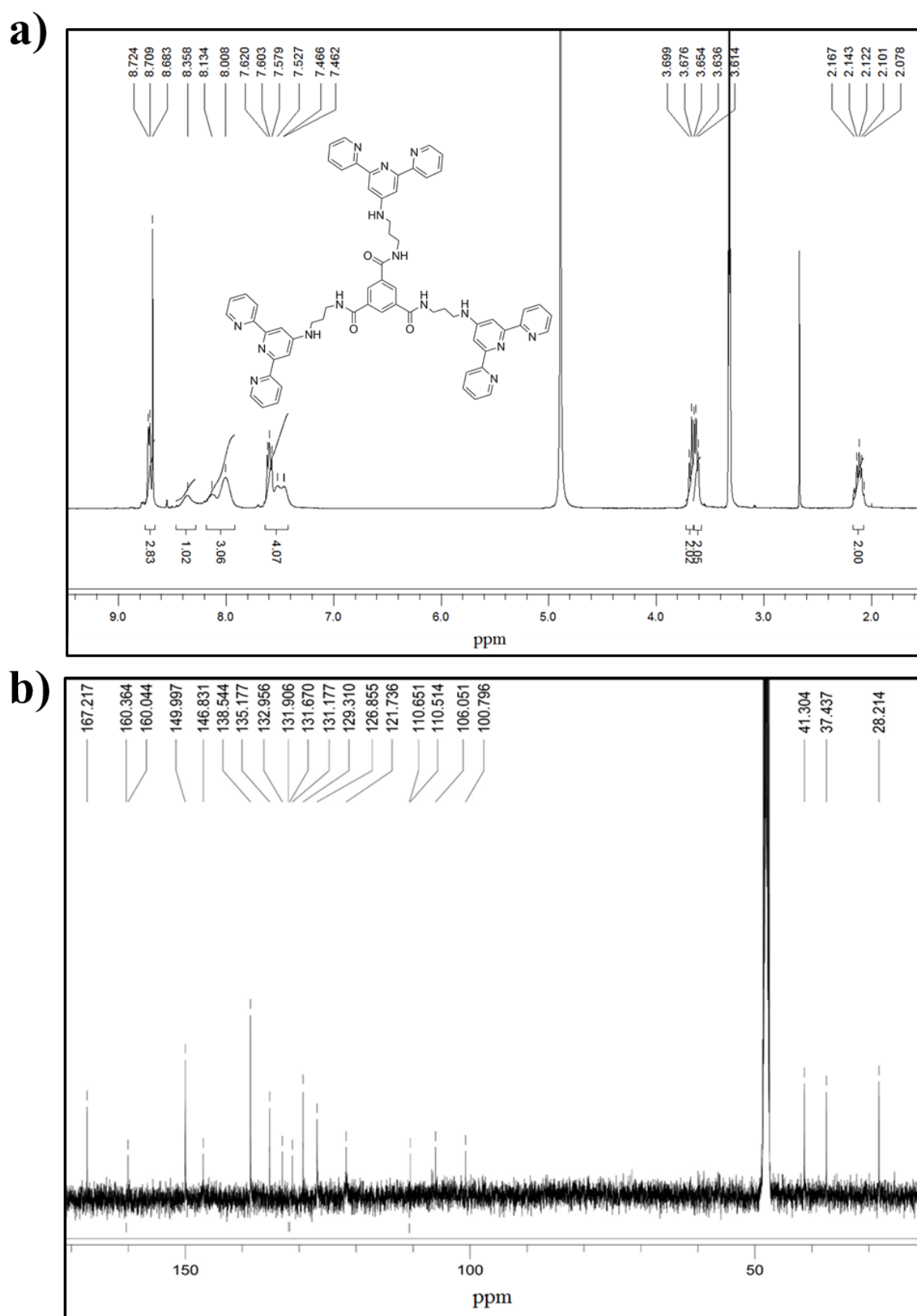




**Fig. S12.** Fluorescence spectra of BT<sub>3</sub> (10 μM) in DMSO/water mixture (1:99 v/v) upon addition of spiked Zn<sup>2+</sup> (2.0-10 μM) in human urine.



**Fig. S13.** a)  $^1\text{H}$  NMR spectrum of **4** (300 MHz,  $\text{CDCl}_3$ ). b)  $^{13}\text{C}$  NMR spectrum of **4** (125 MHz,  $\text{CDCl}_3$ ).



**Fig. S14.** a)  $^1\text{H}$  NMR spectrum of **BT**<sub>3</sub> (300 MHz,  $\text{CD}_3\text{OD}$ ). b)  $^{13}\text{C}$  NMR spectrum of **BT**<sub>3</sub> (125 MHz,  $\text{CD}_3\text{OD}$ ).

## References

1. S. H. Jung, J. Jeon, H. Kim, J. Jaworski, J. H. Jung, *J. Am. Chem. Soc.*, **2014**, *136*, 6446-6452.