Electronic Supplementary Material (ESI) for RSC Advances.

A smart copper (Ⅱ) responsive binuclear gadolinium (Ⅲ) complex based magnetic resonance imaging contrast agent

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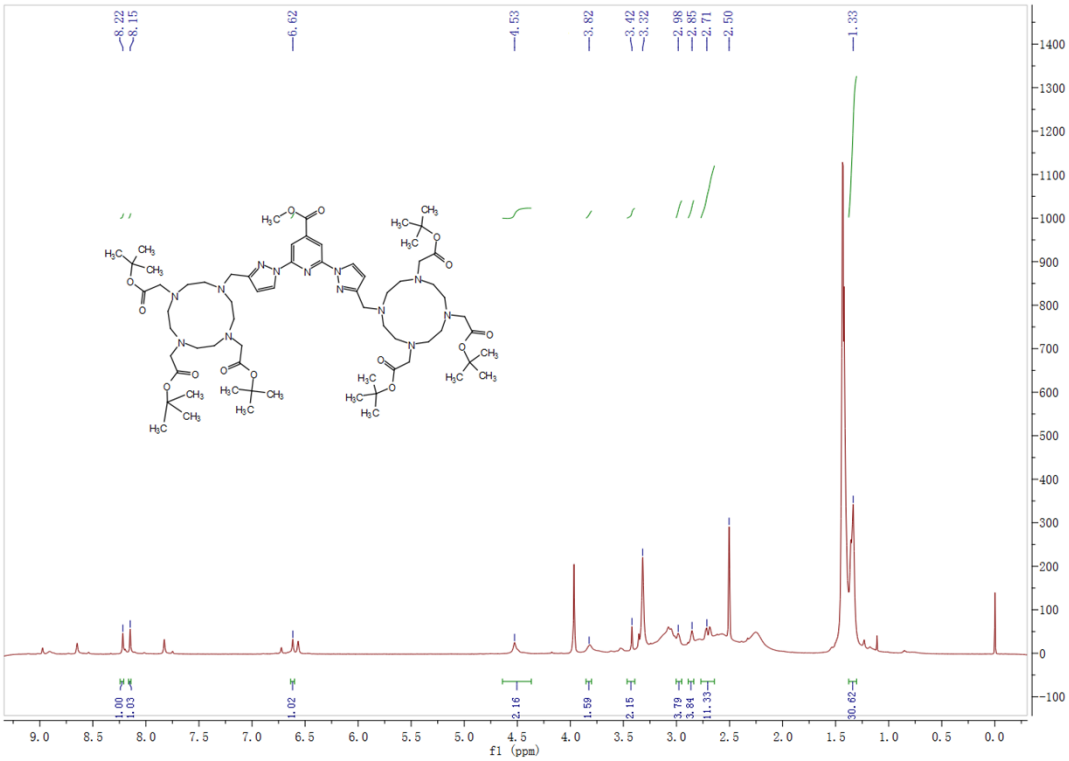


Fig. S1 ^{1}H NMR spectrum of Compound 3 in DMSO (600 MHz).

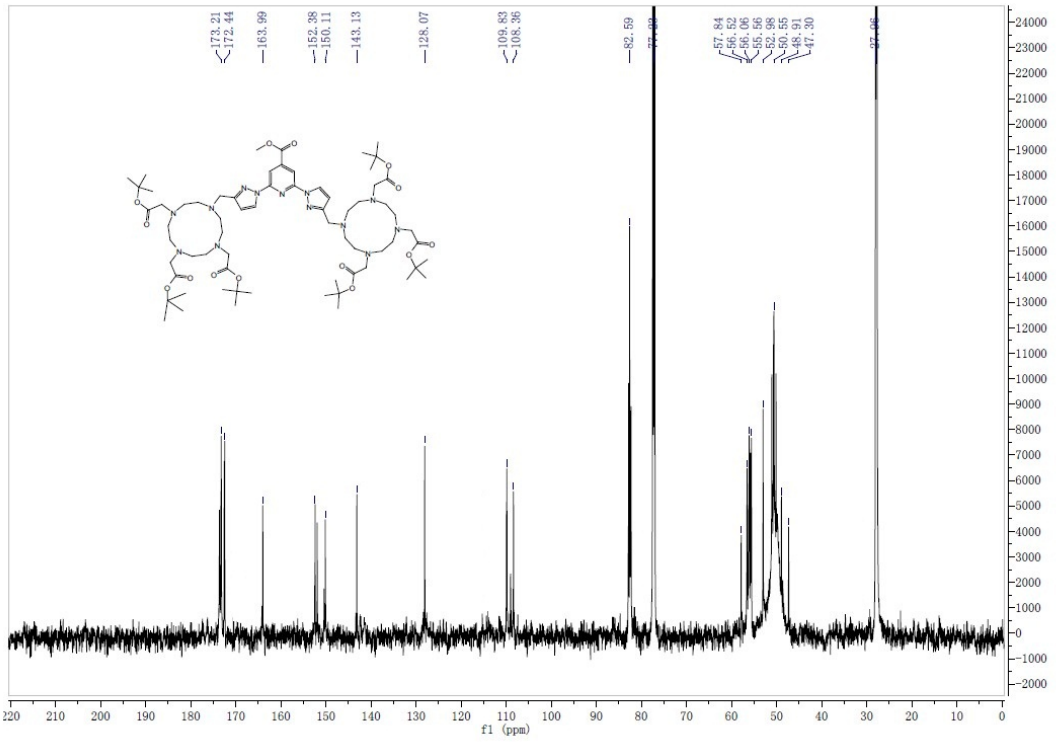
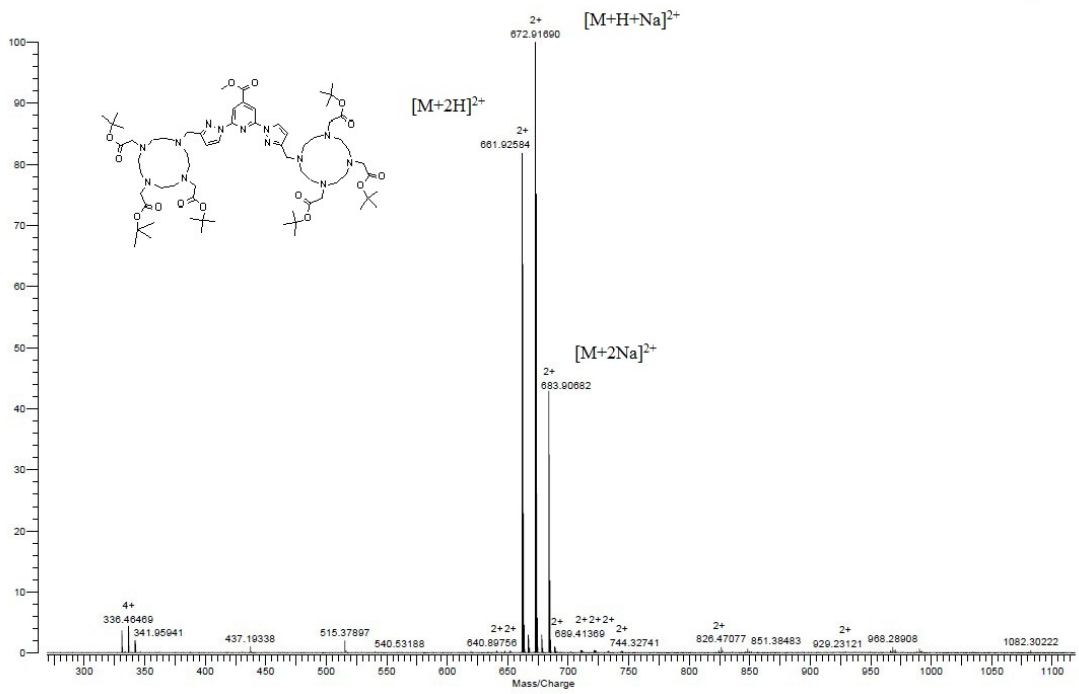


Fig. S2 ^{13}C NMR spectrum of Compound 3 in $CDCl_3$ (151 MHz).



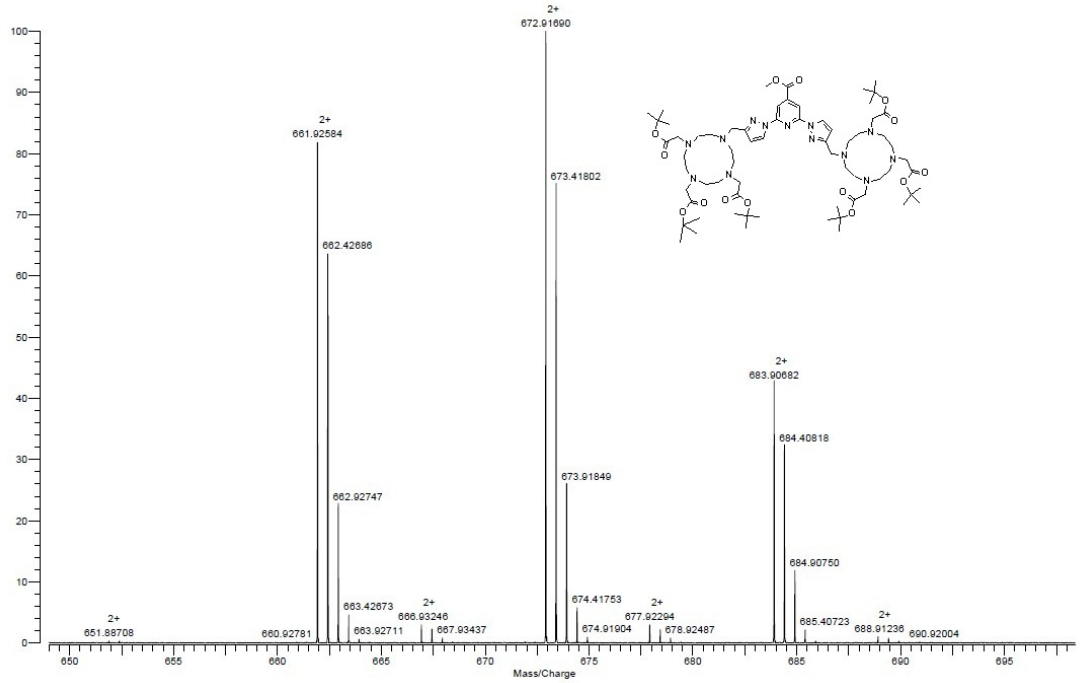


Fig. S3 HRMS (ESI) spectrum and expanded view of **Compound 3**. The peaks at *m/z* = 661.92584, 672.91690, and 683.90682 correspond to $[M + 2H]^{2+}$ (calc. 661.92650), $[M + H + Na]^{2+}$ (calc.672.91747), and $[M + 2Na]^{2+}$ (calc. 683.90844) respectively.

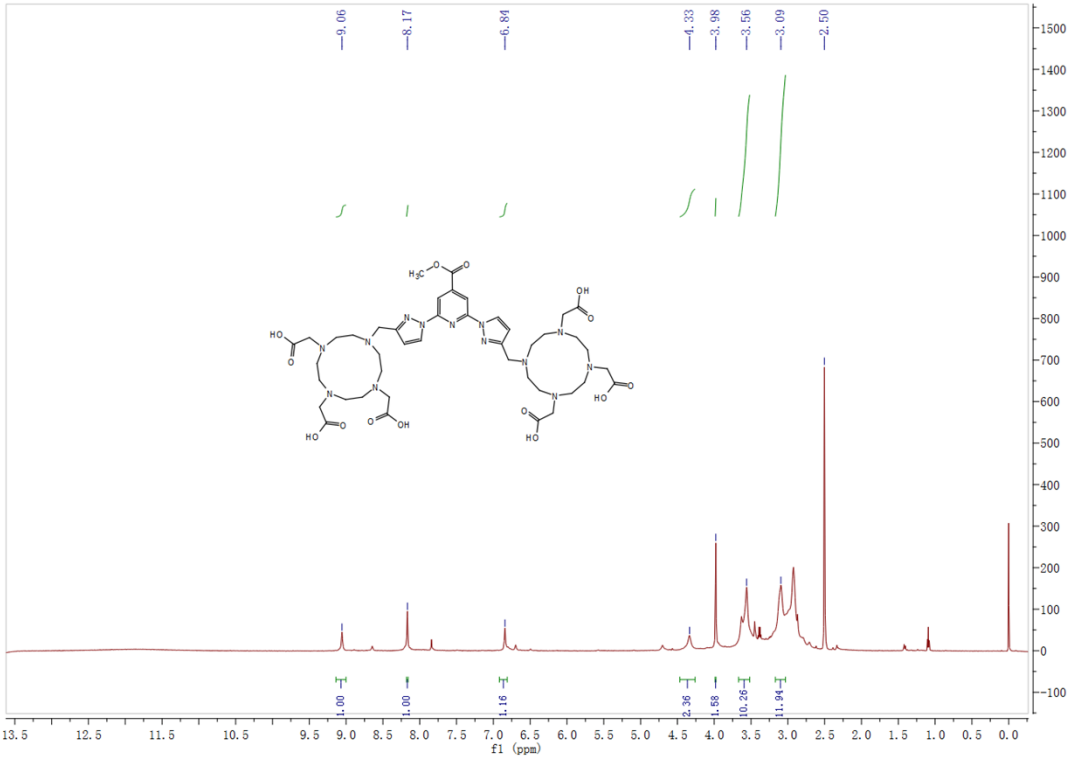


Fig. S4 ^{1}H NMR spectrum of Compound 4 in DMSO (600 MHz).

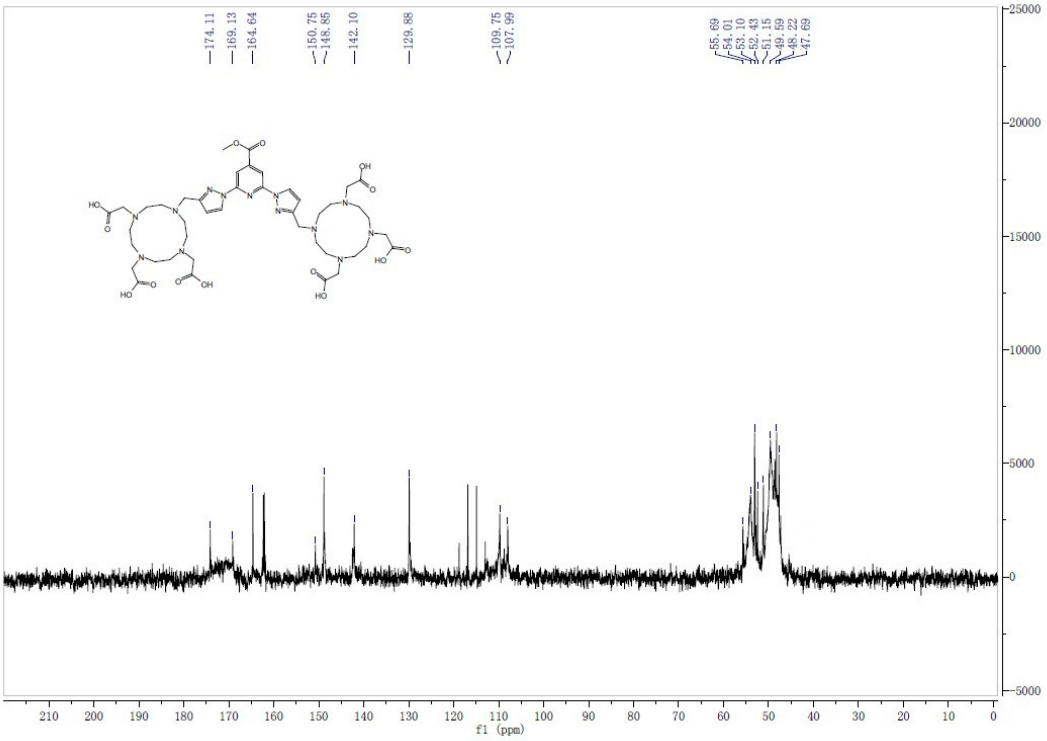


Fig. S5 ^{13}C NMR spectrum of Compound 4 in D_2O (151 MHz).

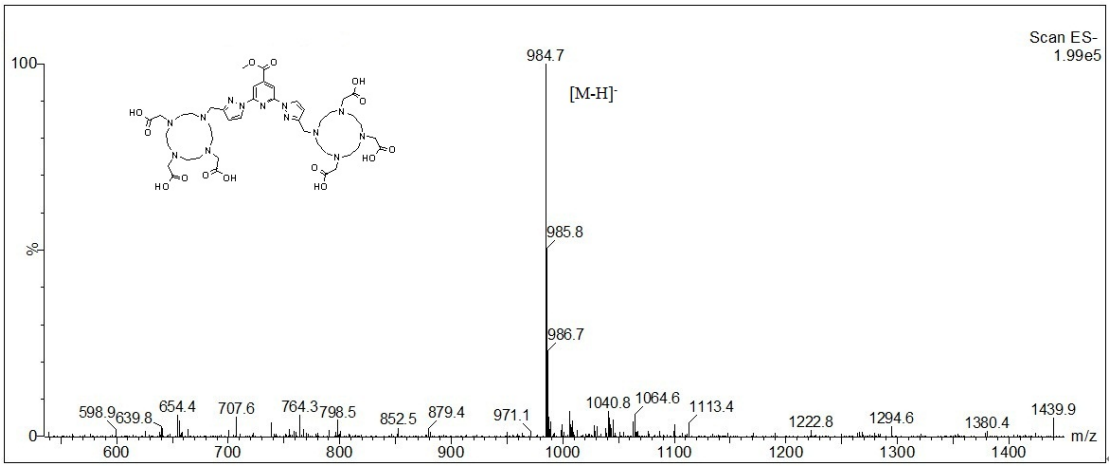


Fig. S6 MALDI-TOF-MS spectrum of **Compound 4**. The peak at *m/z* = 984.7 correspond to $[M - H]^-$ (calc. 984.46).

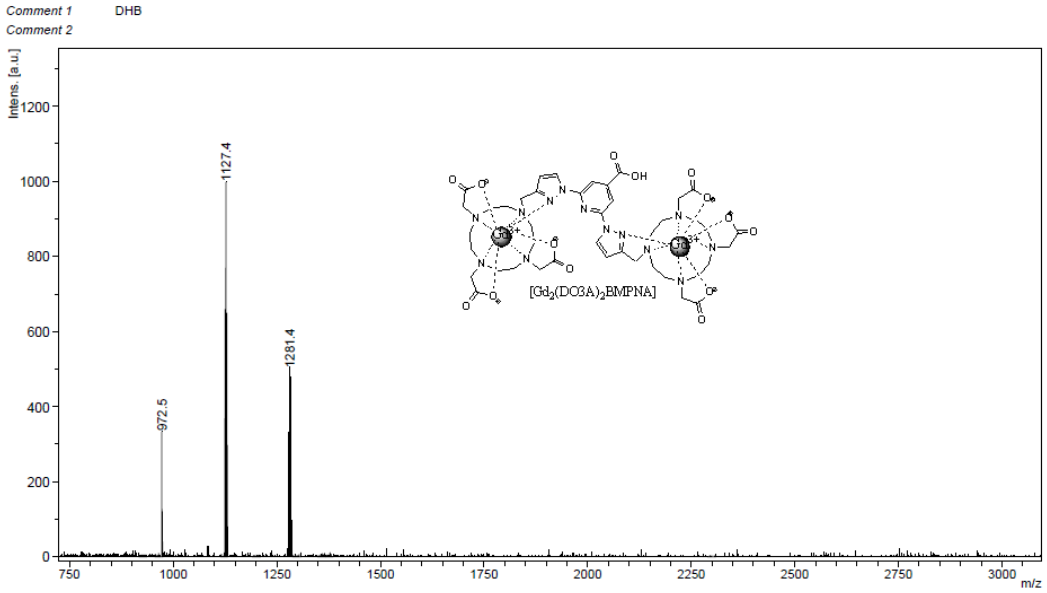


Fig. S7 MALDI-TOF-MS spectrum of **[Gd_2(DO3A)$_2$BMPNA]**. The peak at *m/z* = 1281.4 correspond to $[M + H]^+$ (calc. 1281.46).

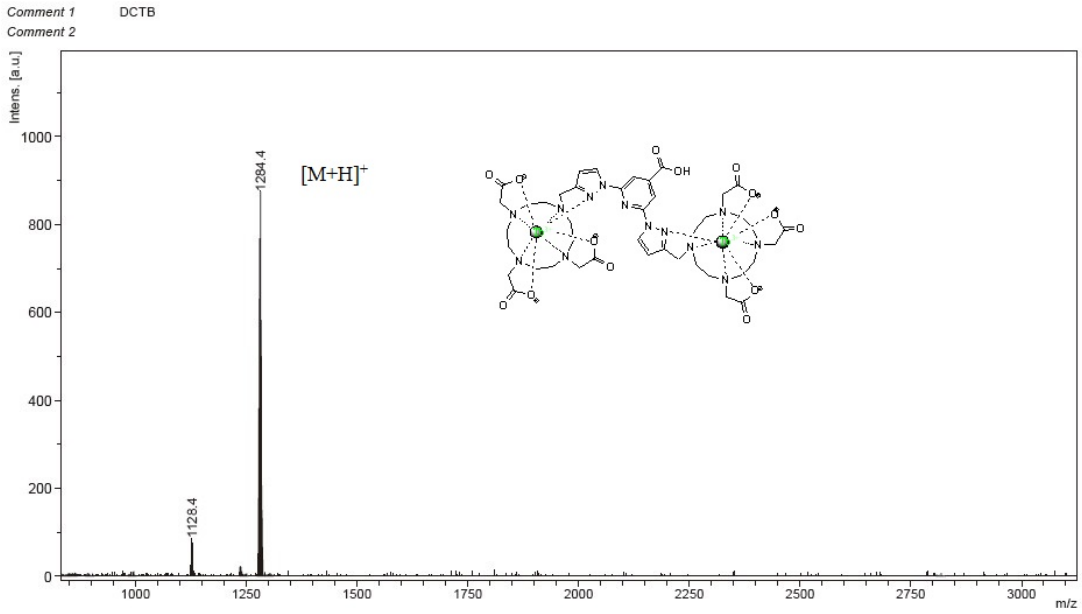


Fig. S8 MALDI-TOF-MS spectrum of **[Tb_2(DO3A)$_2$BMPNA]**. The peak at *m/z* = 1284.4 correspond to $[M + H]^+$ (calc. 1284.3).

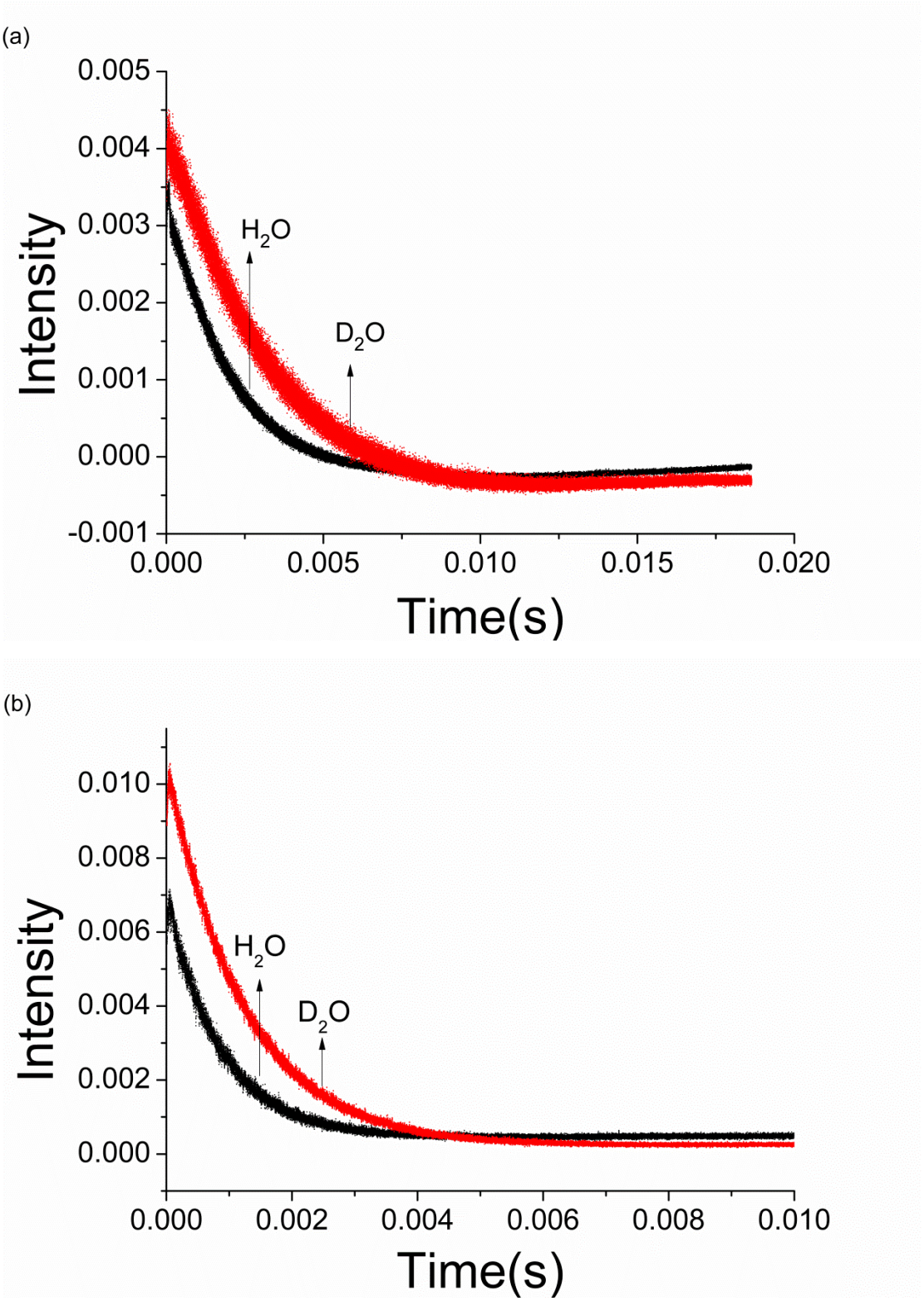


Fig. S9 (a) Luminescence decay of **[Tb_2(DO3A)$_2$BMPNA]** in H_2O and D_2O without addition of Cu^{2+};

(b) Luminescence decay of **[Tb_2(DO3A)$_2$BMPNA]** in H_2O and D_2O with addition of Cu^{2+}.

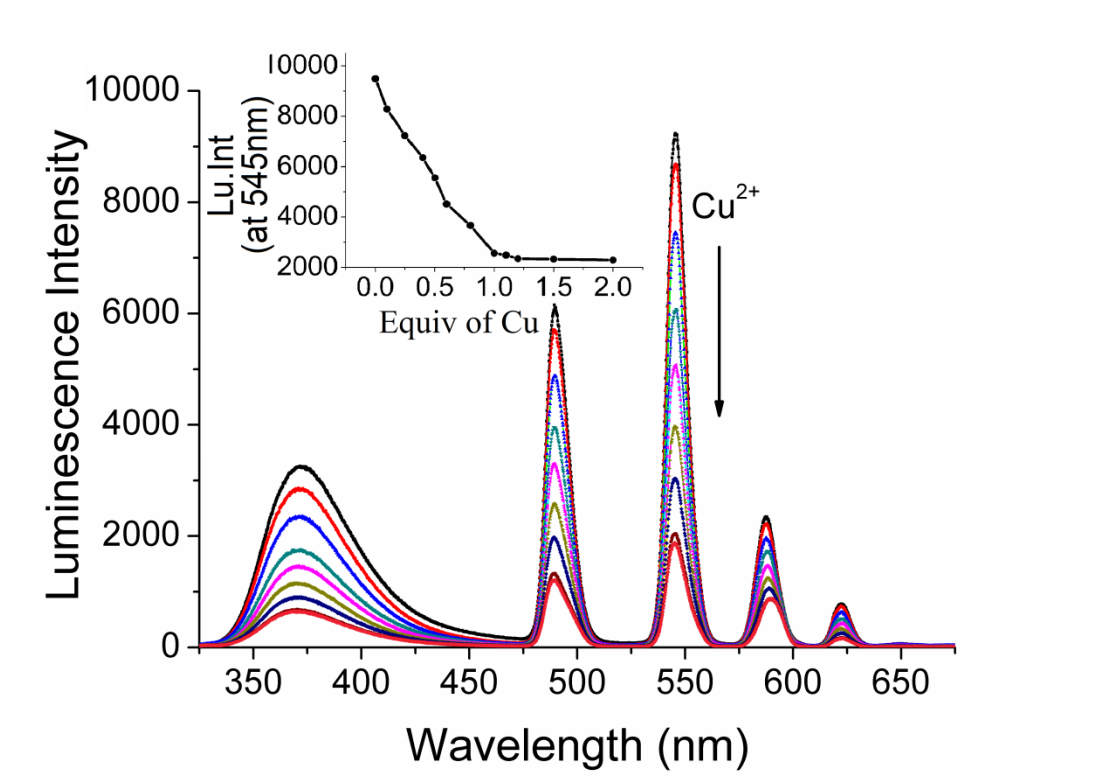


Fig. S10 Luminescence spectra of **[Tb_2(DO3A)$_2$BMPNA]** (20 μM) upon addition of different concentrations of Cu^{2+} (0-2 equiv.) in HEPES-buffered (pH 7.4, 100 mM) aqueous solutions. Excitation wavelength: 295 nm. Inset shows the luminescence at 545 nm as a function of Cu^{2+} concentration suggesting a 1:1 binding ratio between **[Tb_2(DO3A)$_2$BMPNA]** and Cu^{2+}.

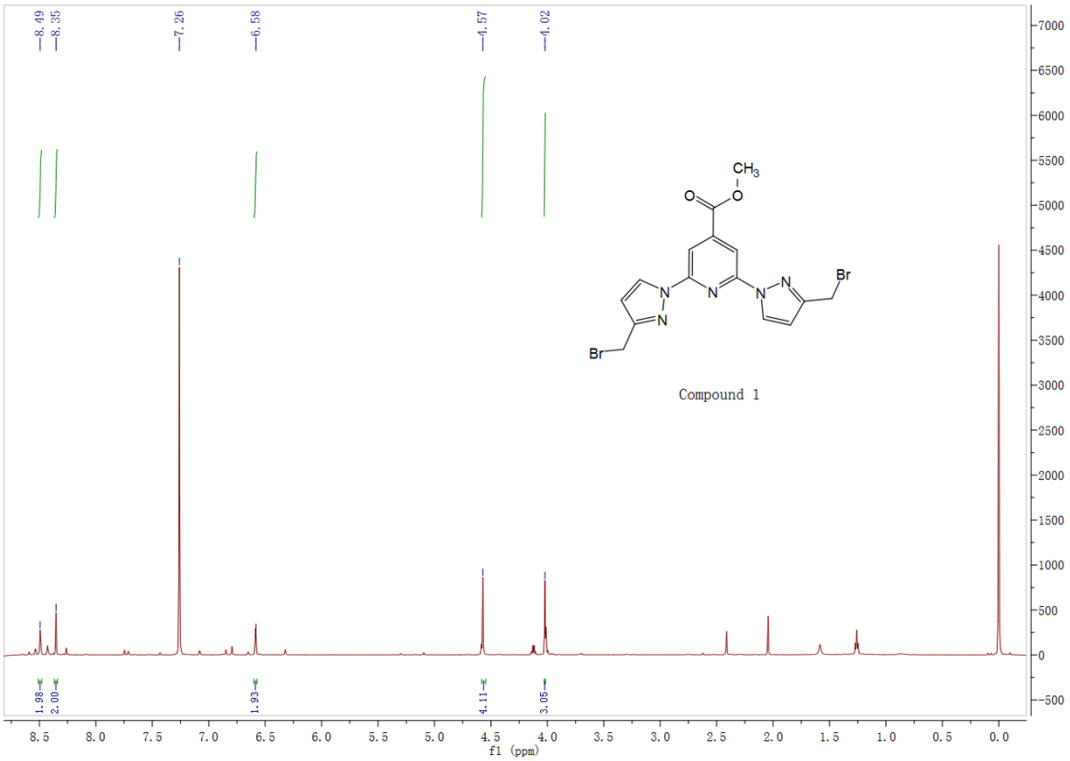


Fig. S11 ^{1}H NMR spectrum of Compound 1 in $CDCl_3$ (600 MHz).

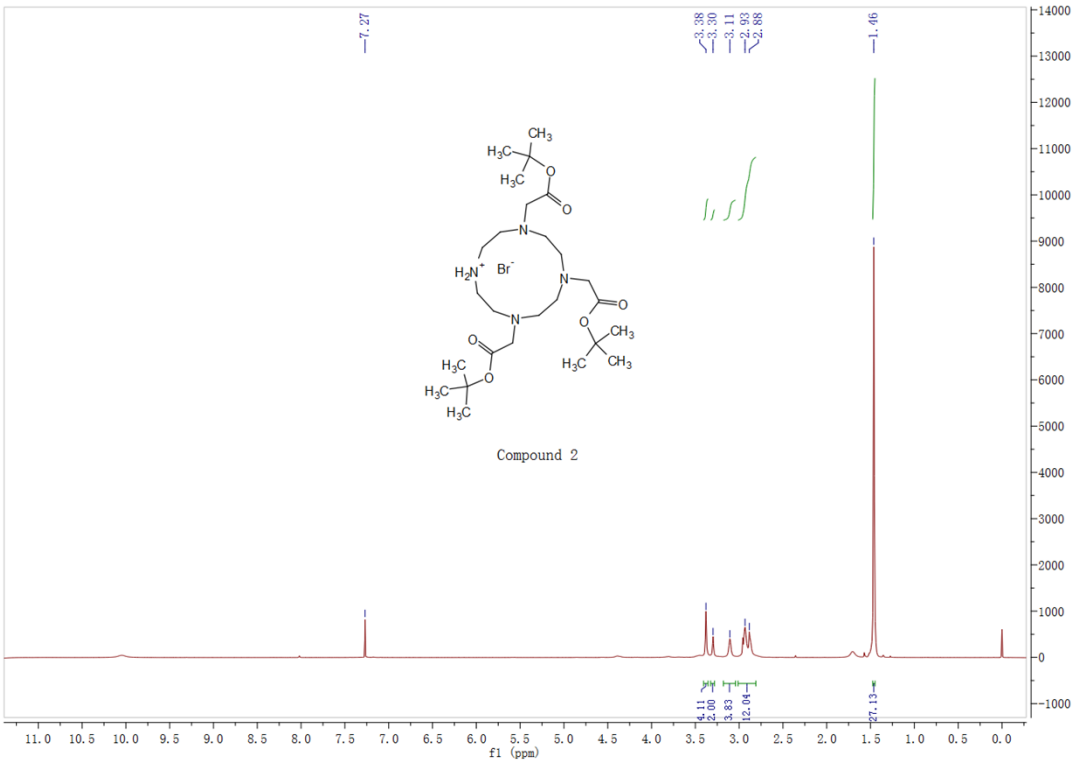


Fig. S12 ^{1}H NMR spectrum of Compound 2 in $CDCl_3$ (600 MHz).

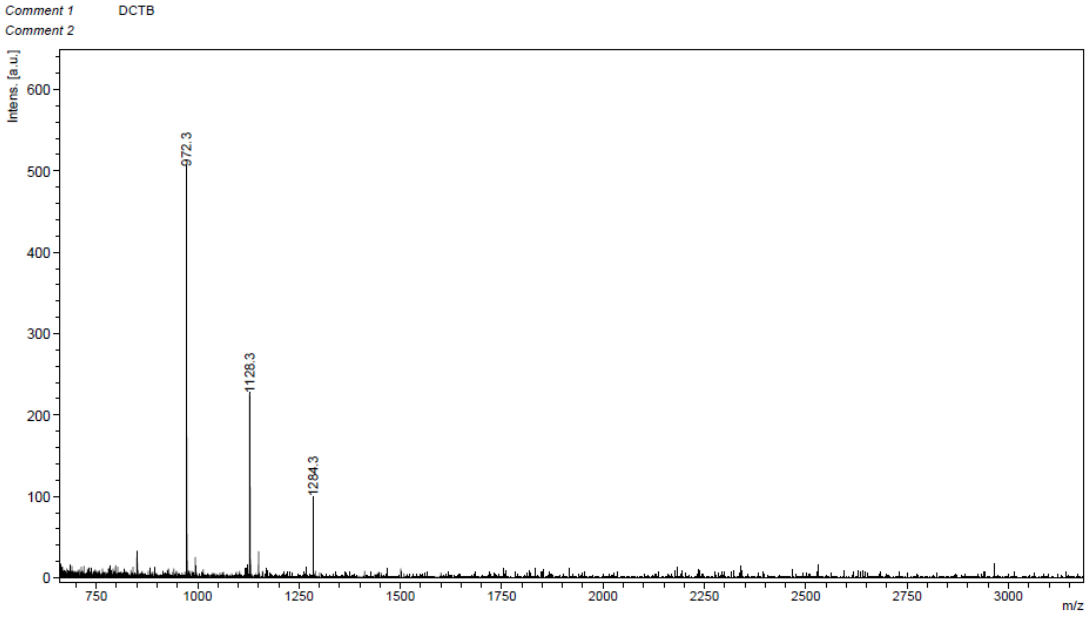


Fig. S13 MALDI-TOF-MS spectrum of **[Gd_2(DO3A)$_2$BMPNA]** in the presence of Zn^{2+} at room temperature after 7 days . No metal-ion exchange was observed.

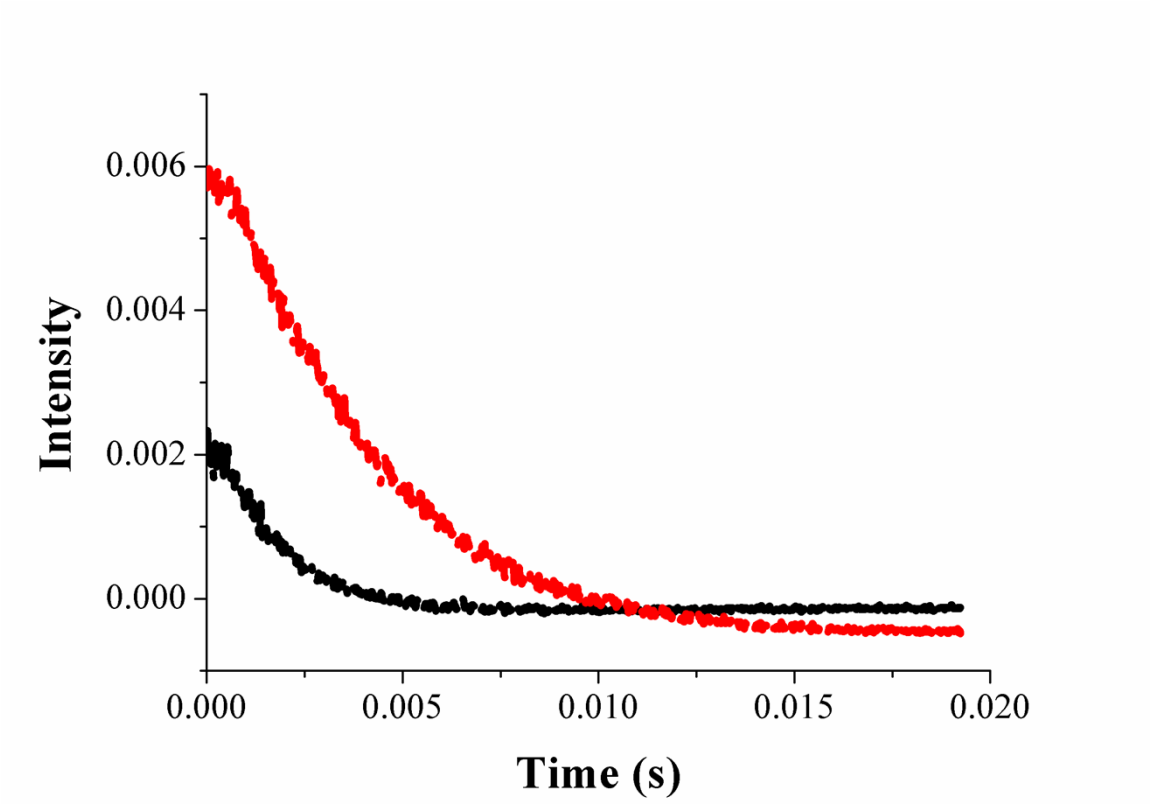


Fig. S14 Luminescence decay of **[Tb_2(DO3A)$_2$BMPNA]** in H_2O (black) and D_2O (red) with addition of Cu^{2+} and phosphate.