Electronic Supplementary Material (ESI) for Dalton Transactions

Gadolinium(III) Complex based Dual-Modal Probe for MRI and Fluorescence Sensing Fluoride ion in Aqueous Medium and *in Vivo*

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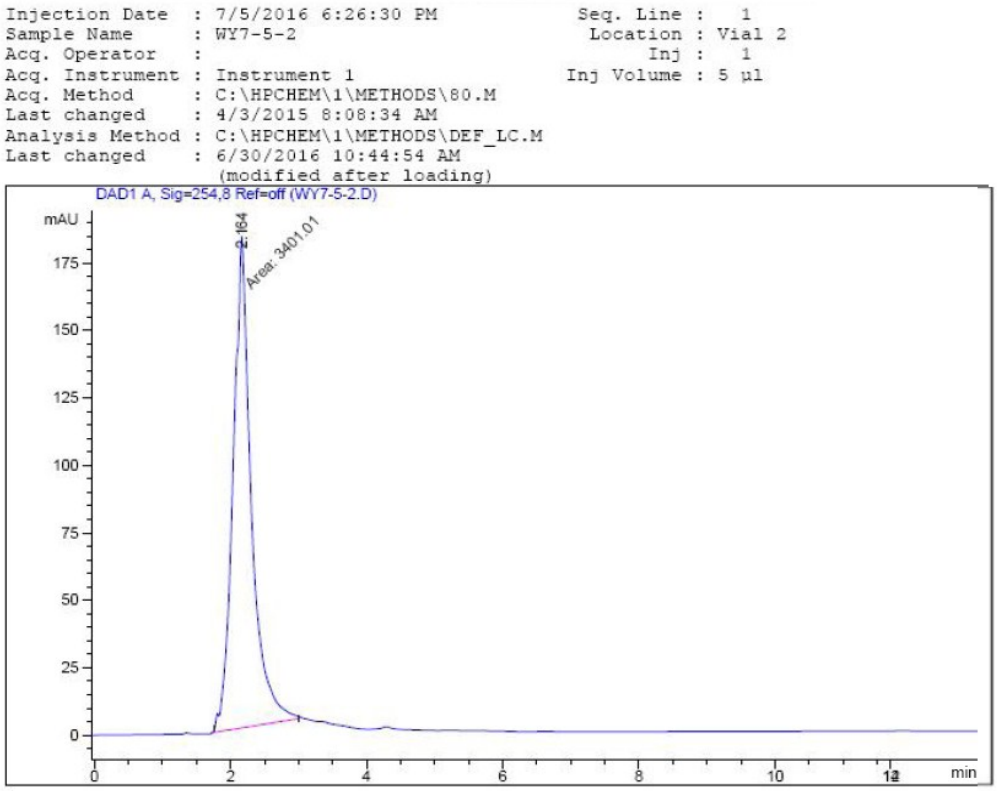

Fig. S1 HPLC of Gd(TTA)$_3$-**DPPZ** (methanol as eluent).

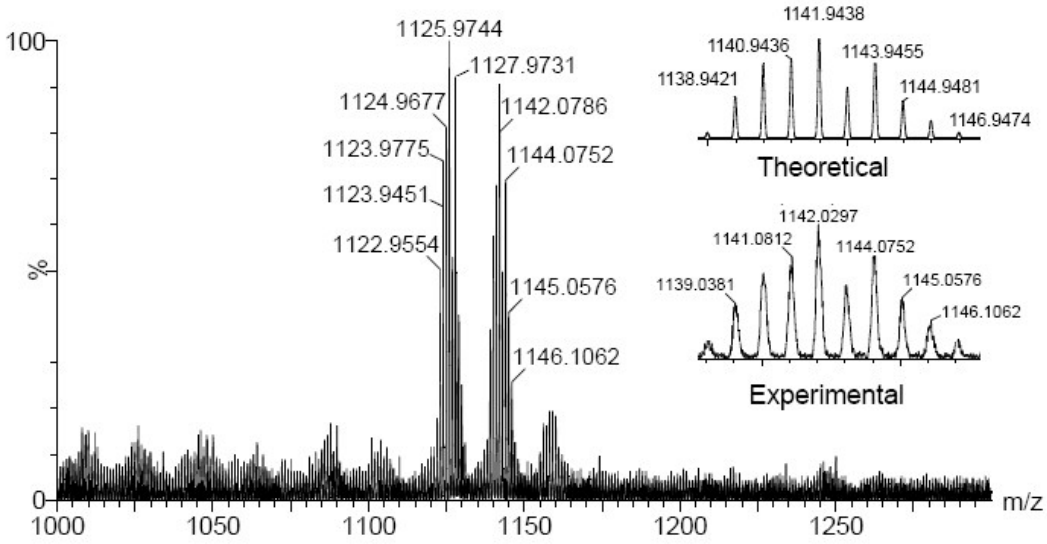

Fig. S2 ESI-MS spectrum of Gd(TTA)$_3$-**DPPZ**.

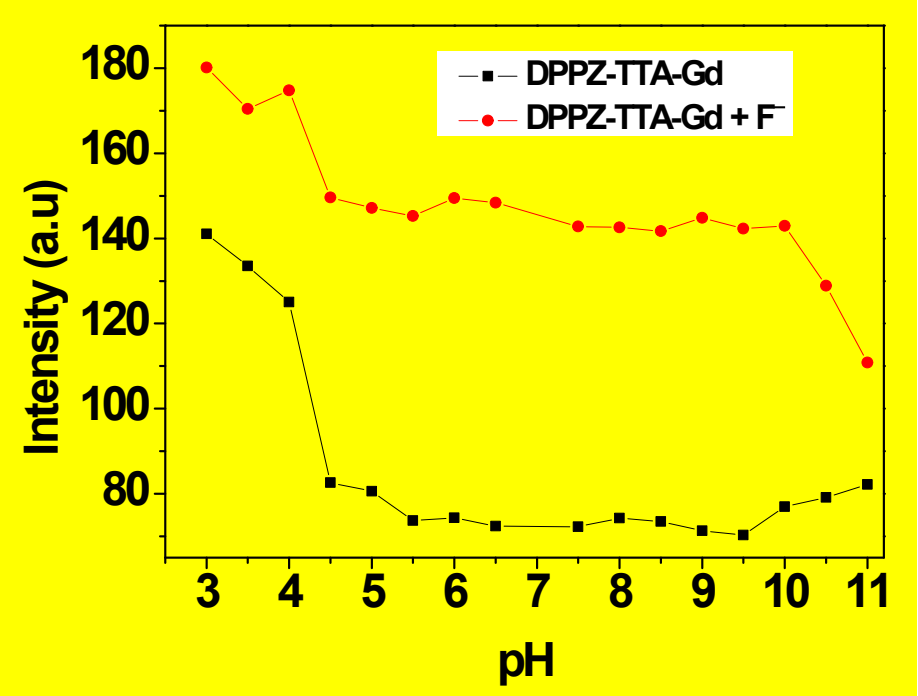

Fig. S3 Variations of fluorescence intensity of Gd(TTA)$_3$-**DPPZ** (10 μM) at 420 nm in aqueous solution in the presence and absence of fluoride ion (0.7 mM) as a function of pH. Eexcitation at 340 nm.

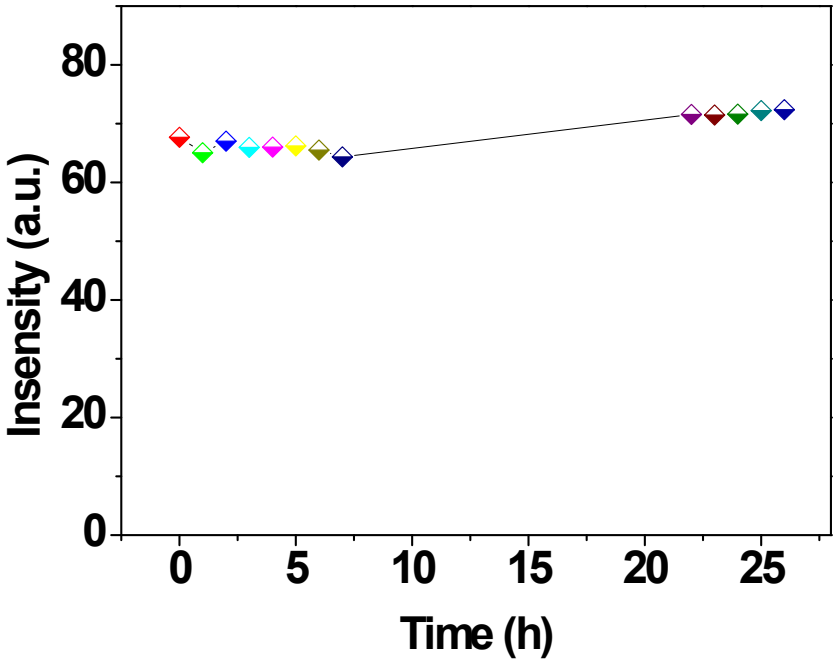

Fig. S4 Fluorescence spectra of Gd(TTA)$_3$-**DPPZ** (10 μM) at different time in H_2O (THF: H_2O = 5:5, pH = 7.4). The intensities were recorded at 420 nm, excitation at 340 nm.

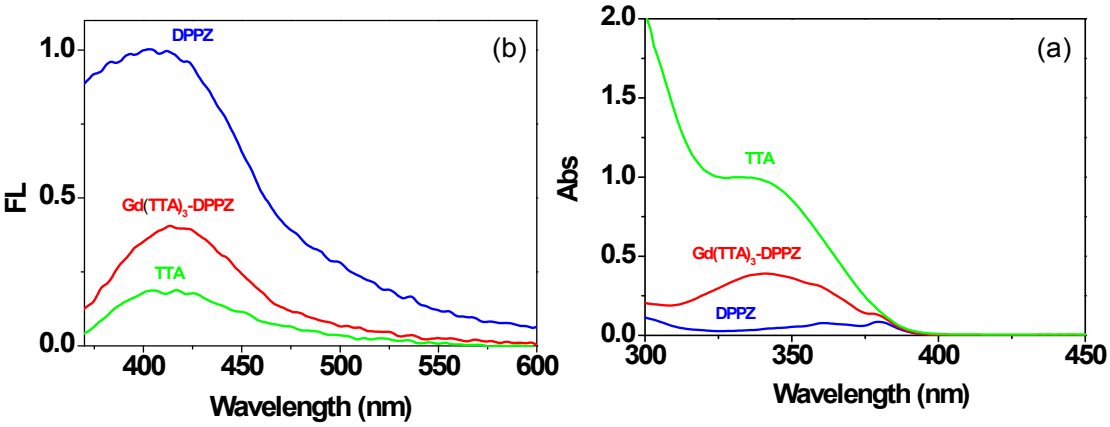

Fig. S5 Normalized fluorescence emission and UV-Vis absorption spectra of TTA, DPPZ, and Gd(TTA)$_3$-**DPPZ** (10 μM) in H_2O (THF: H_2O = 5:5, pH = 7.4).

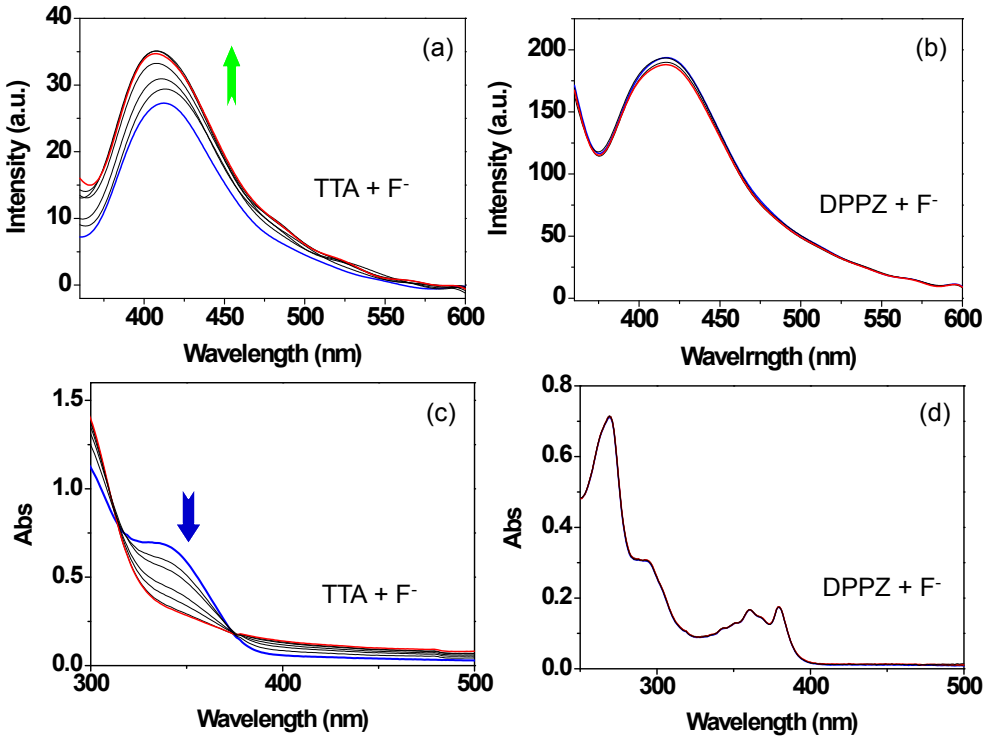

Fig. S6 Changes in fluorescence (a), (b), and absorption (c), (d) spectra of TTA and DPPZ in the presence of increased concentrations of fluoride in H_2O (THF: H_2O = 5:5, pH = 7.4).

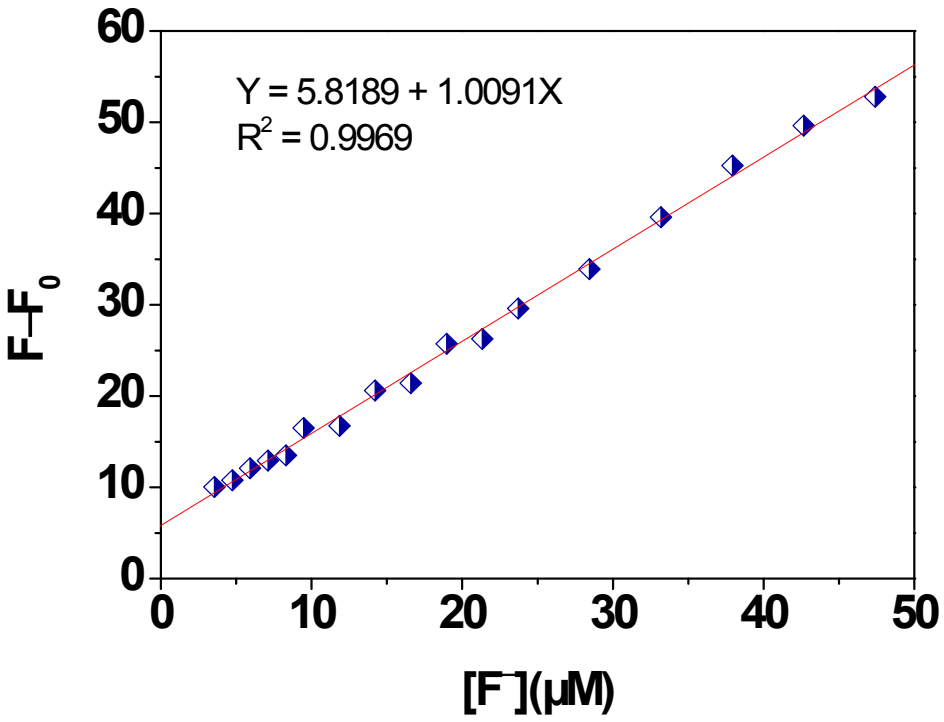

Fig. S7 The linear fluorescence responses of Gd(TTA)$_3$-**DPPZ** (2 μM) in H_2O (THF: H_2O = 5:5, pH = 7.4) versus low concentration fluoride concentration (0–50 μM) at 420 nm. Excitation was performed at 340 nm.

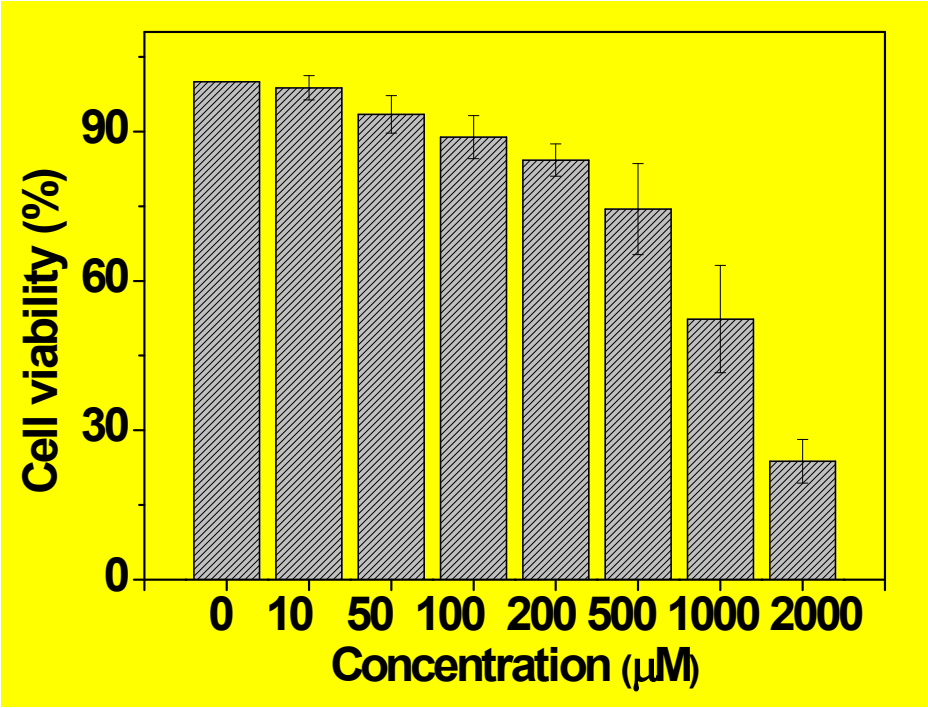

Fig. S8 MDA-MB-231 cell viability values (%) assessed using an MTT proliferation test versus incubation concentrations of Gd(TTA)$_3$-**DPPZ**.

MTT cell viability assays. MTT assay was utilized to investigate the cytotoxicity of $Gd(TTA)_3$-**DPPZ**. MDA-MB-231 cells were seeded at a density of 5×10^4 cells/mL in a 96-well micro-assay culture plate and growth 24 h at 37 °C in a 5% CO_2 incubator. $Gd(TTA)_3$-**DPPZ** in fresh culture medium was added into each well with different concentrations from 10 to 2000 μM. Control wells were prepared by the addition of culture medium, and wells containing culture media without cells were used as blanks. After incubation at 37 °C in a 5% CO_2 incubator for 6 h, cell culture medium was removed and cells were washed three times with PBS. Then, 100 μL, 0.5 mg/mL MTT solution in PBS was added to each well, and the cells were incubated for another 4 h. The excess MTT solution was then carefully removed from each well, and the formed formazan was dissolved in 100 μL of DMSO (dimethyl sulfoxide). The optical density of each well was then measured at a wavelength of 540 nm using a microplate reader (Bio-Rad, xMark). The results from the five individual experiments were averaged. The following formula was used to calculate the viability of cell growth:

Vialibity (%) = (mean of absorbance value of treatment group–blank)/(mean absorbance value of control–blank) × 100.

Table S1. Comparisons of the sensitivity of Gd(TTA)$_3$-**DPPZ** with other reported fluoride ion fluorescence probes

Sensing mechanisms	**No.**	**Probe Name**	**Solution**	**Fluorescence sensitivity**
Hydrogen bonding	Refer. 1	Sensor **1**	CH_3CN : HEPES (0.02 M, pH 7.2)	1.21 μM
	Refer. 2	**R1**	DMF	0.4 μM
	Refer. 3	**probe 1**	DMSO	1.8 μM
	Refer. 4	**1-Naphthaldoxime 1**	DMSO/Water (99/1)	50 *ppb*
	Refer. 5	**S2**	DMSO	10 *ppm*
	Refer. 6	**[Eu.L$_1$]$^+$**	HEPES (pH 7.4)	0.2 μM
Fluoroborate complexation	Refer. 7	**BAPTA**-Ca	MOPS buffer (pH 7.0).	0.3 mM
	Refer. 8	**[Zr(H$_2$O)$_2$edta]–flavonol**	Acetate buffer (pH 5.0);	3 μM (60 *ppb*)
	Refer. 9	**RF**	Ethanol/Water (2/3)	1.6 μM
Fluoride mediated desilylation	Refer. 10	**Sensor 1**	CH_3CN	1.0 μM
	Refer. 11	Probe **FP**	CH_3CN	19 *ppb*
	Refer. 12	**BW-F-204**	PBS (pH 7.4)	18 μM
	Refer. 13	**QF**	PBS (pH 7.4)	0.5 μM
	Refer. 14	**FP-1**	HEPES-CH_3CN (1:5, pH 7.4)	0.59 μM
	This paper	Gd(TTA)$_3$-**DPPZ**	THF: H_2O (5:5, pH = 7.4)	**70 nM (1.33 *ppb*)**

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