

Electronic Supplementary Material (ESI) for Dalton Transactions

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

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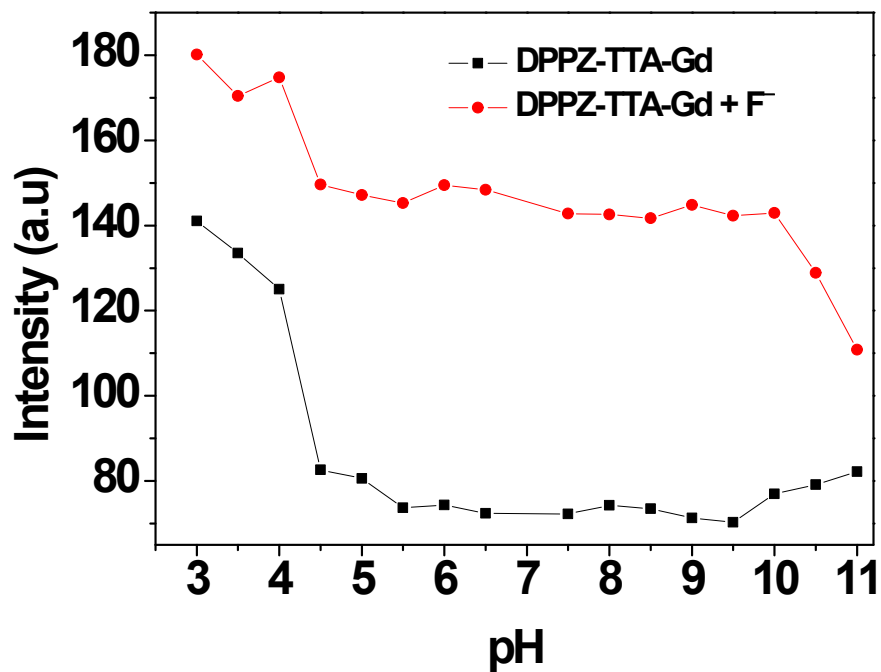


Fig. S3 Variations of fluorescence intensity of Gd(TTA)₃-DPPZ (10 μM) at 420 nm in aqueous solution in the presence and absence of fluoride ion (0.7 mM) as a function of pH. Eexcitation at 340 nm.

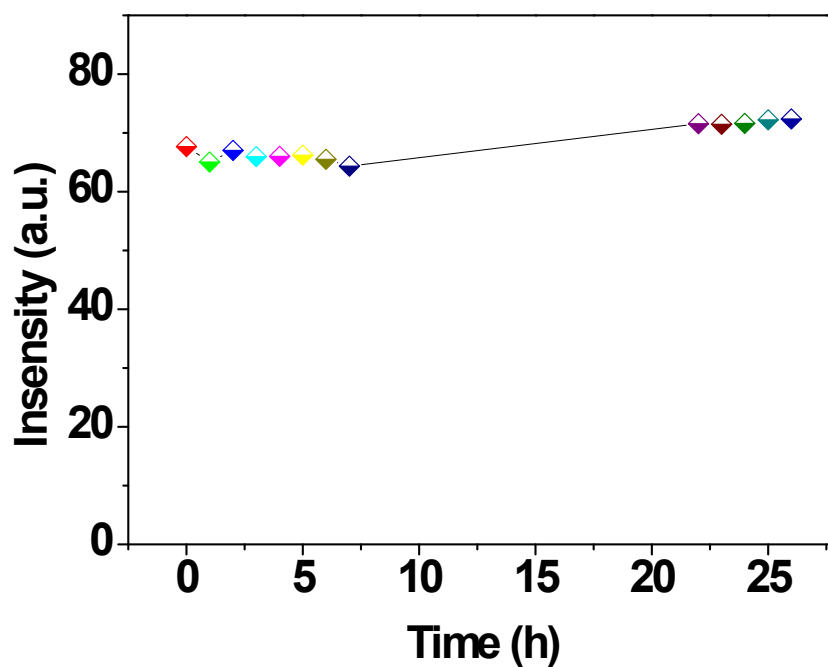


Fig. S4 Fluorescence spectra of Gd(TTA)₃-DPPZ (10 μM) at different time in H₂O (THF: H₂O = 5:5, pH = 7.4). The intensities were recorded at 420 nm, excitation at 340 nm.

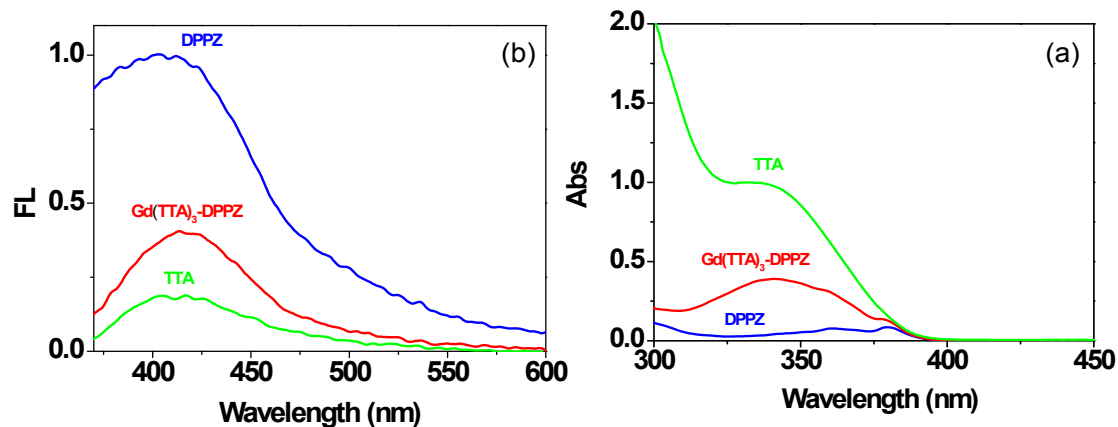


Fig. S5 Normalized fluorescence emission and UV-Vis absorption spectra of TTA, DPPZ, and $\text{Gd}(\text{TTA})_3\text{-DPPZ}$ (10 μM) in H_2O (THF: H_2O = 5:5, pH = 7.4).

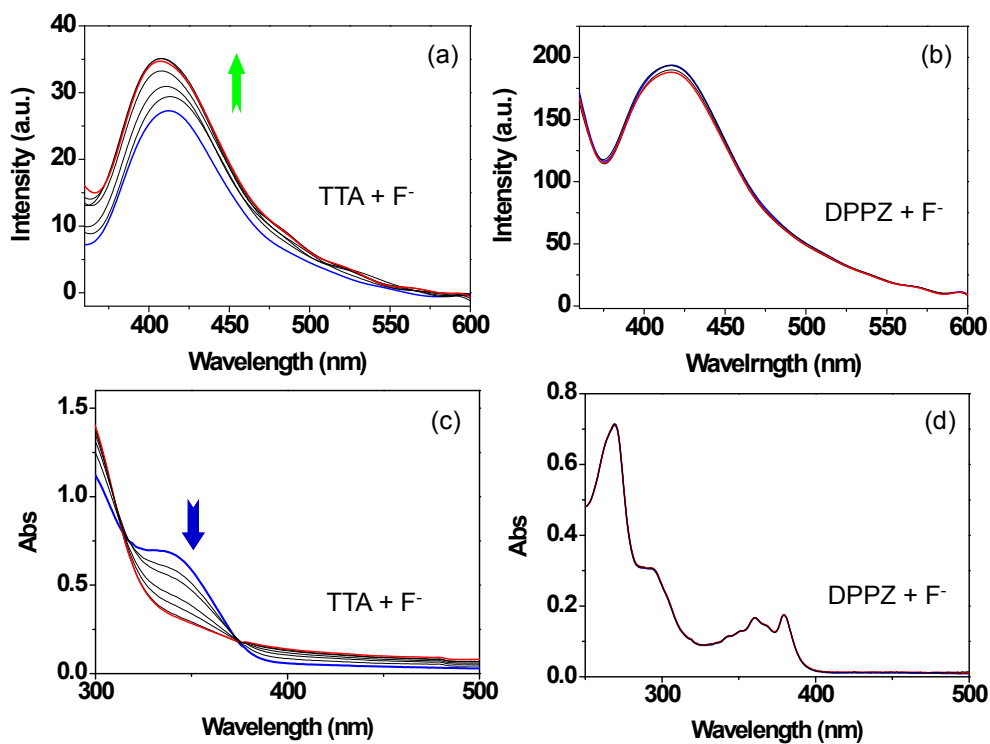


Fig. S6 Changes in fluorescence (a), (b), and absorption (c), (d) spectra of TTA and DPPZ in the presence of increased concentrations of fluoride in H_2O (THF: H_2O = 5:5, pH = 7.4).

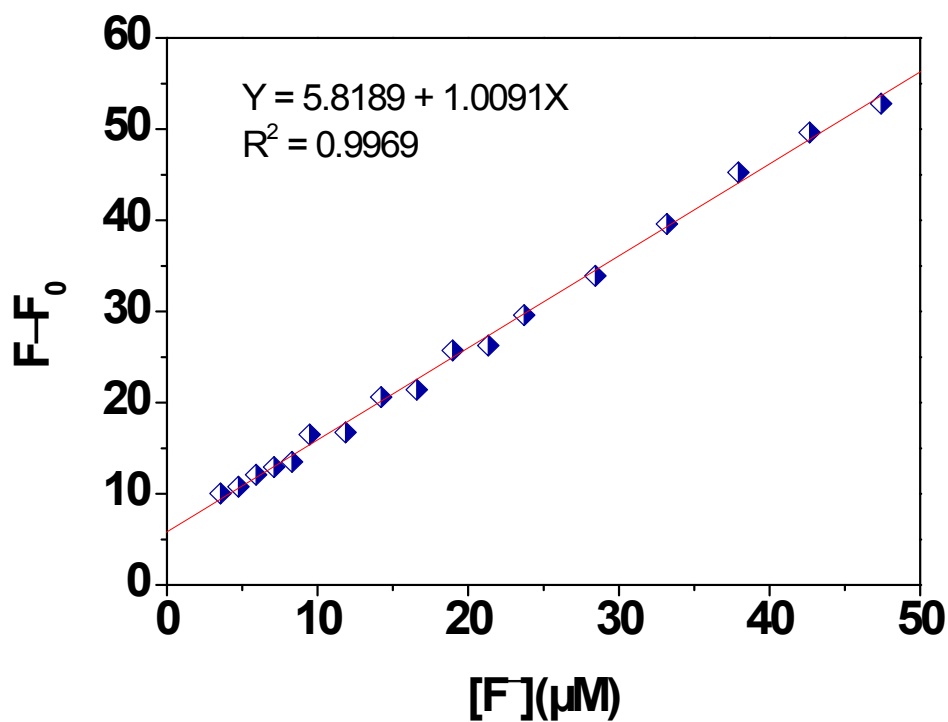


Fig. S7 The linear fluorescence responses of Gd(TTA)₃-DPPZ (2 μM) in H₂O (THF: H₂O = 5:5, pH = 7.4) versus low concentration fluoride concentration (0–50 μM) at 420 nm. Excitation was performed at 340 nm.

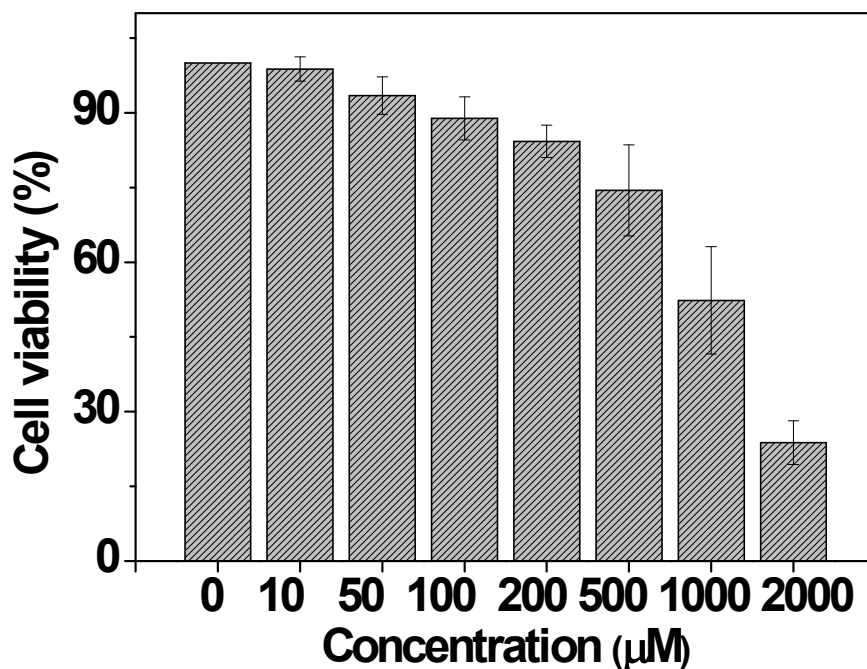


Fig. S8 MDA-MB-231 cell viability values (%) assessed using an MTT proliferation test versus incubation concentrations of Gd(TTA)₃-DPPZ.

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% CO₂ 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% CO₂ 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:

Viability (%) = (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 ₃ CN : 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 ₃ CN	1.0 μM
	Refer. 11	Probe FP	CH ₃ CN	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 ₃ CN (1:5, pH 7.4)	0.59 μM
	This paper	Gd(TTA) ₃ -DPPZ	THF: H ₂ O (5:5, pH = 7.4)	70 nM (1.33 ppb)

References:

1. A. K. Mahapatra, R. Maji, K. Maiti, S. S. Adhikari, C. D. Mukhopadhyay and D. Mandal, *Analyst*, 2014, **139**, 309–317.
2. C. Parthiban and K. P. Elango, *Sensors and Actuators B*, 2015, **215**, 544–552.
3. M. Yu, J. Xu, C. Peng, Z. Li, C. Liu and L. Wei, *Tetrahedron*, 2016, **72**, 273–278.
4. C. B. Rosen, D. J. Hansen and K. V. Gothelf, *Org. Biomol. Chem.*, 2013, **11**, 7916–7922.
5. M. S. Kumar, S. L. A. Kumar and A. Sreekanth, *Anal. Methods*, 2013, **5**, 6401–6410.
6. S. J. Butler, *Chem. Commun.*, 2015, **51**, 10879–10882.

7. S. Rochat and Kay Severin, *Chem. Commun.*, 2011, **47**, 4391–4393.
8. Y. Takahashi, D. A. P. Tanaka, H. Matsunaga and T. M. Suzuki, *J. Chem. Soc., Perkin Trans.*, 2002, **2**, 759–762.
9. Y. Mia, Z. Caob, Y. Chen, S. Long, Q. Xie, D. Liang, W. Zhu and J. Xiang, *Sensors and Actuators B*, 2014, **192**, 164– 172
10. Y. Bao, B. Liu, F. Du, J. Tian, H. Wang and R. Bai, *J. Mater. Chem.*, 2012, **22**, 5291–5294.
11. S. Zhang, J. Fan, S. Zhang, J. Wang, X. Wang, J. Du and X. Peng, *Chem. Commun.*, 2014, **50**, 14021–14024.
12. Y. Zheng, Y. Duan, K. Ji, R.-L. Wang and B. Wang, *RSC Adv.*, 2016, **6**, 25242–25245.
13. W. Hu, L. Zeng, Y. Wang, Z. Liu, X. Ye and C. Li, *Analyst*, 2016, DOI: 10.1039/C6AN00905K.
14. M. Yoo, S. Park and H.-J. Kim, *RSC Adv.*, 2016, **6**, 19910–19915.