

Supporting information for:

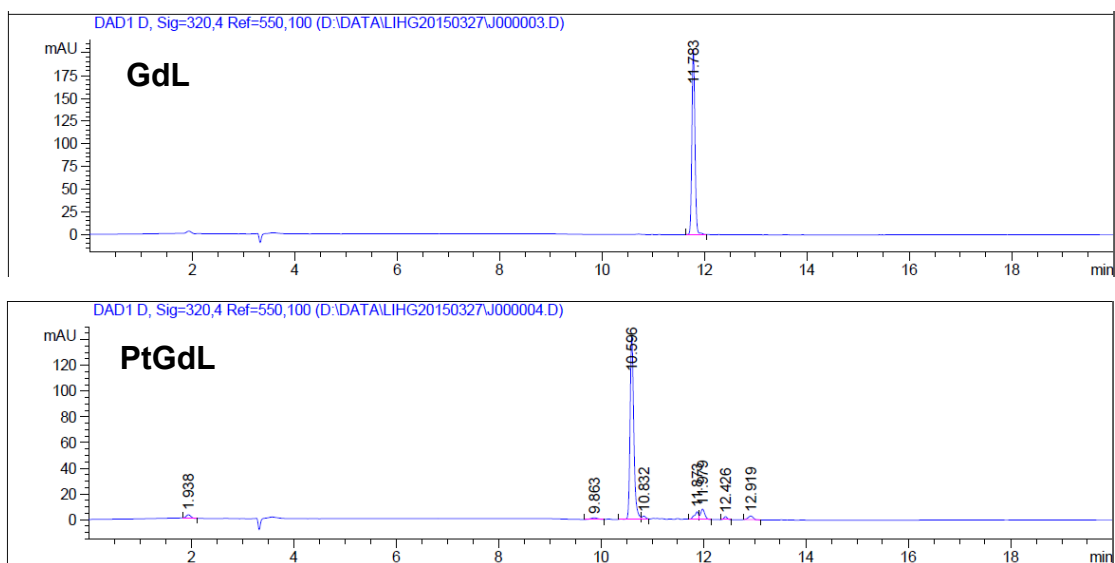
## **Gadolinium and Platinum in Tandem: Real-time Multi-Modal**

### **Monitoring of Drug Delivery by MRI and Fluorescence Imaging.**

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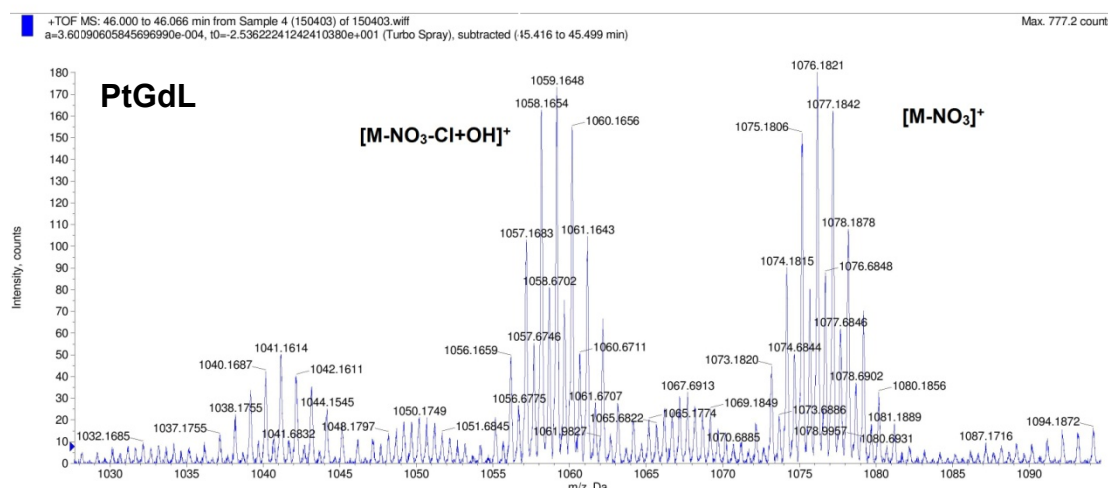
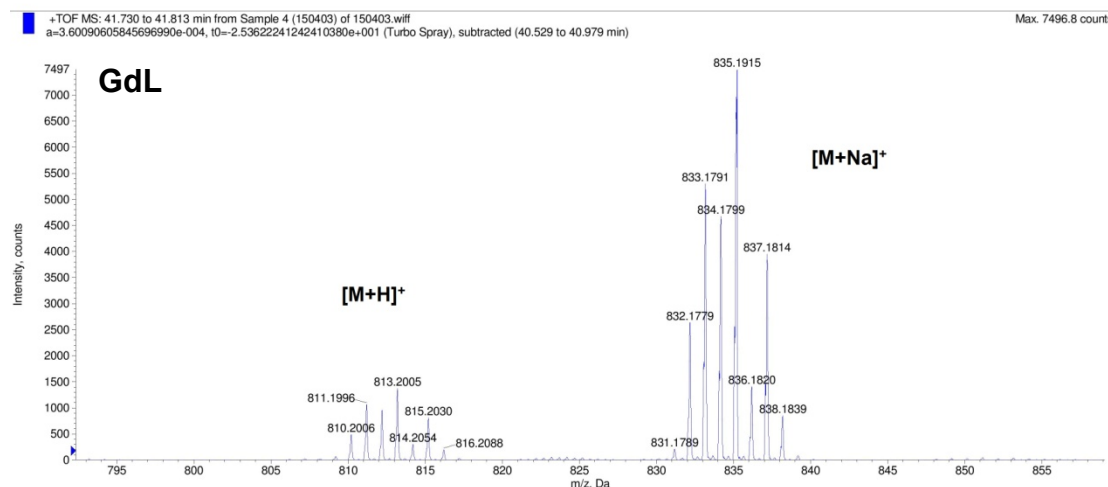
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**Figure S1.** HPLC spectra of the **GdL** and **PtGdL**. Experimental conditions: Agilent ZORBAX SB-C18 Stable Bond Analytical 4.6 X 150 mm 5-micron column, solvent gradient show in table S1.

**Table S1.** Solvent gradient of the HPLC for characterization of **GdL** and **PtGdL**.

Time /min	0.05% TFA in water /%	0.05% TFA in CH <sub>3</sub> CN /%	Flow rate/ mLmin <sup>-1</sup>
0	90	10	1.0
5	90	10	1.0
15	60	40	1.0
20	90	10	1.0



**Figure S2.** ESI-HRMS spectra of **GdL** and **PtGdL**. **GdL**: calcd. for  $C_{34}H_{37}GdN_7O_7$   $[M + H]^+$  813.1995, found 813.2005, for  $C_{34}H_{36}GdN_7NaO_7$   $[M + Na]^+$  835.1815, found 835.1915. **PtGdL**: HRMS (+ESI) m/z calcd. for  $C_{34}H_{42}ClGdN_9O_7Pt$   $[M - NO_3]^+$  1076.1784, found 1076.1821, for  $C_{34}H_{43}ClGdN_9O_8Pt$   $[M - NO_3 - Cl + OH]^+$  1058.2123, found 1058.1654.

**Table S2.** Photophysical properties and relaxivity of **PtGdL** and **GdL**.

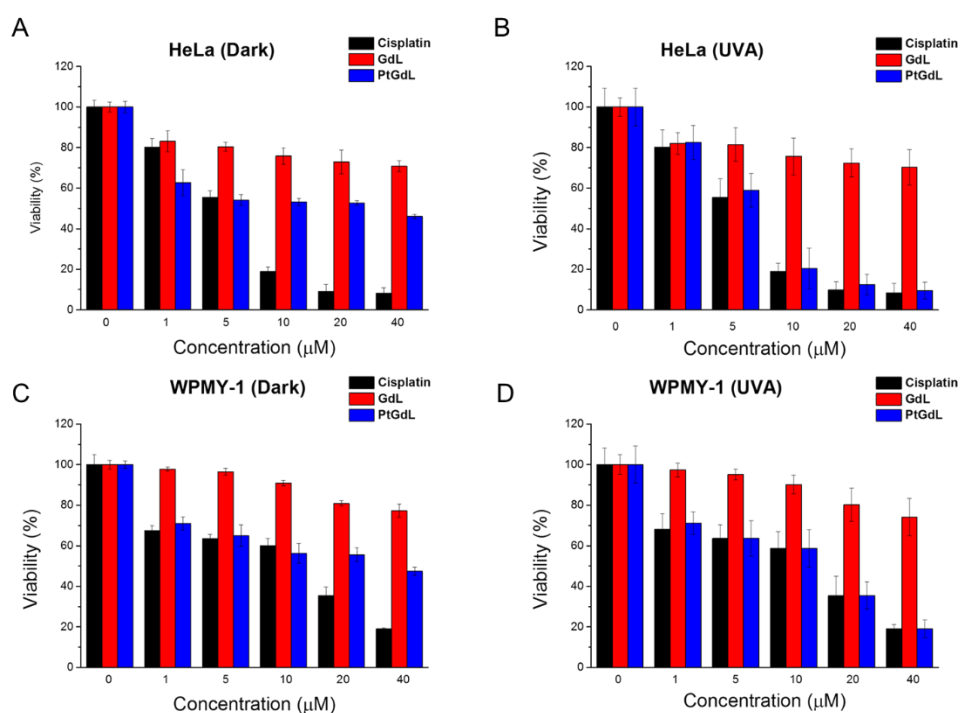
Complex	$\lambda_{\max}/\text{nm}$ <sup>[a]</sup>	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$ <sup>[a]</sup>	$q \pm 0.2$ <sup>[b]</sup>	$\phi/\%$ <sup>[d]</sup>	$r_1/\text{mM}^{-1}\text{s}^{-1}$ <sup>[e]</sup>
<b>PtGdL</b>	327	22300	1.0 <sup>[c]</sup>	< 0.1	29.4
<b>GdL</b>	324	20000	1.0	3	23.1

a) Absorption coefficient in H<sub>2</sub>O, 298 K; b) Coordination number of water molecules, the q value of **GdL** was determined by comparison of the emission lifetime of europium(III) analogue of **GdL**, **EuL** in D<sub>2</sub>O and H<sub>2</sub>O, which is reported in our previous work. (*Chem. Commun.* **2015**, 51, 14022; *J. Chem. Soc., Perkin Trans.* **1999**, 2, 493.) c) For **PtGdL** the q value could not be determined by using the same method with **GdL** because **PtEuL** is non-emissive, however **PtGdL** should have the same hydration number ( $q = 1.0 \pm 0.2$ ) as **GdL** due to the similarity of structure. d) Fluorescence quantum yield of the ligand emission of the complexes was determined by integrated sphere methods. (*Chem. Rev.* **2010**, 110, 2729.) e)  $T_1$  relaxivity of the Gd(III) complexes at 10 MHz, 25 °C.

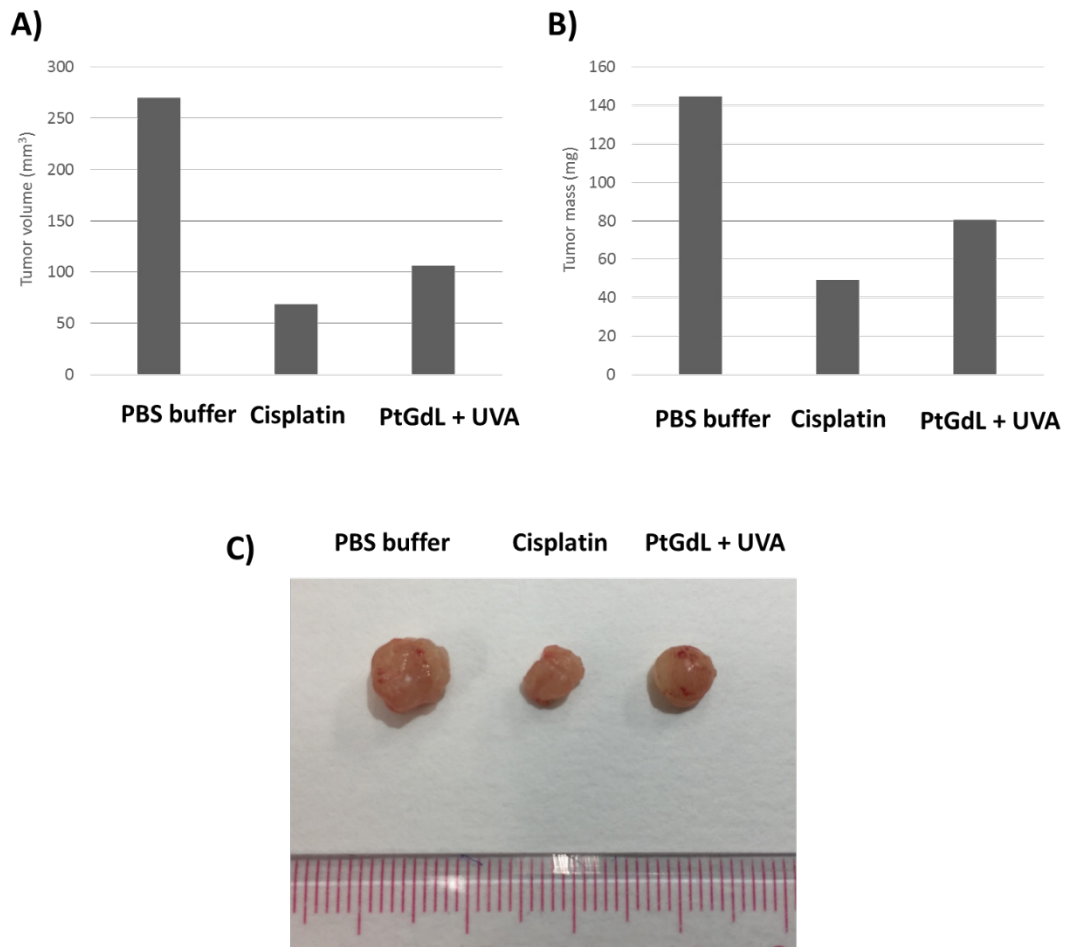
**Table S3.** IC<sub>50</sub> (μM) values of **PtGdL**, **GdL** and cisplatin (as control) in HeLa and WPMY-1 cells under dark and UVA irradiation.<sup>[a]</sup>

Complex	HeLa		WPMY-1	
	Dark IC <sub>50</sub>	UVA <sup>[b]</sup> IC <sub>50</sub>	Dark IC <sub>50</sub>	UVA <sup>[b]</sup> IC <sub>50</sub>
<b>PtGdL</b>	23.6 ± 0.8	3.8 ± 0.7	43.9 ± 1.1	~6.9 ± 1.1
<b>GdL</b>	> 200	> 200	> 200	> 200
<b>Cisplatin</b>	3.3 ± 0.3	3.4 ± 0.7	4.2 ± 0.6	4.1 ± 0.9

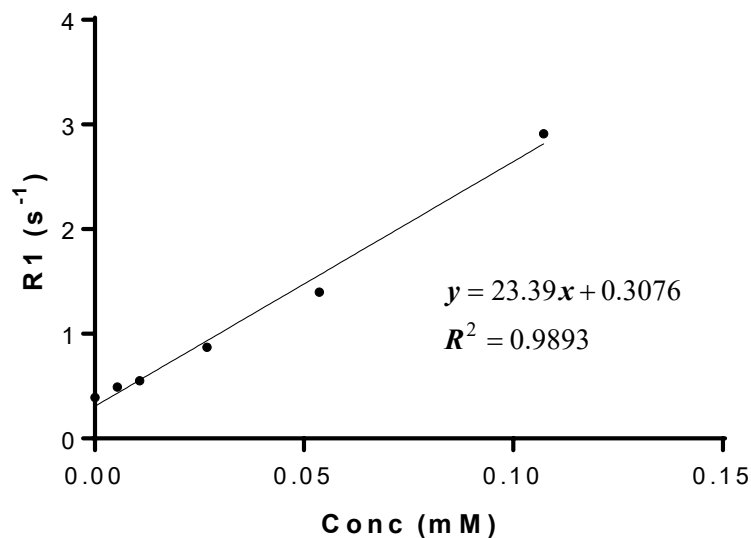
a) Incubation time = 24 hour; b) λ<sub>ex</sub> = 365 nm, light dosage = 1 Jcm<sup>-2</sup>. Raw data shows in Figure S3.



**Figure S3.** Raw data of MTT dark (A and C) and photo (B and D) cytotoxicity in Table S3.



**Figure S4.** *In vivo* tumor inhibition of **PtGdL** with UVA irradiation. A) The volume, (B) mass and the photograph of the tumor after 14 days treatment of the PBS buffer (control), cisplatin (control) and **PtGdL** + UVA.



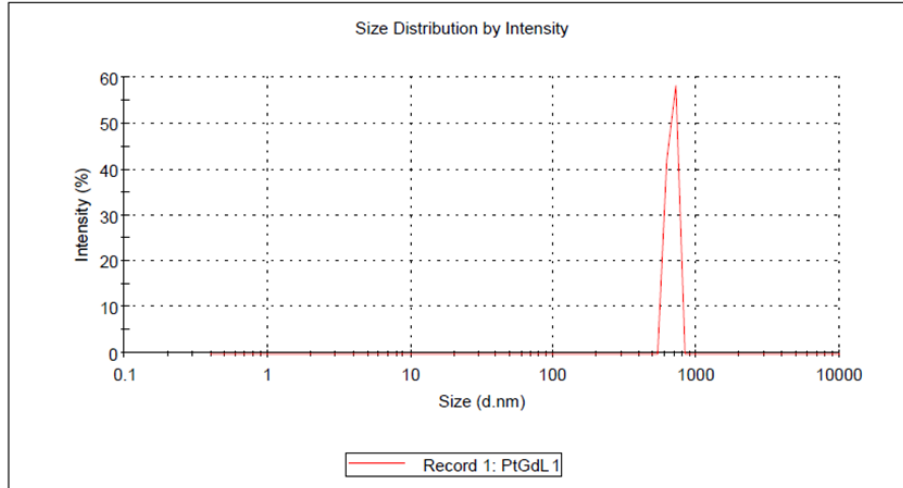
**Figure S5.** The plot of  $R_1$  versus the concentration of **PtGdL** in aqueous solution. Linear fitting of the data gives a relaxivity of **PtGdL** =  $23.4 \text{ mM}^{-1}\text{s}^{-1}$ , at 3T and 25°C.

**Table S4.** Raw data of the  $T_1$  relativity of **PtGdL** at 3T (25°C) in Figure S4.

Conc. <sup>[a]</sup> (mol/L)	$T_1$ (ms) <sup>[b]</sup> ( $\pm$ SD)	$R_1$ (s <sup>-1</sup> ) <sup>[c]</sup>
1.07E-04	343 $\pm$ 13	2.91
5.36E-05	713 $\pm$ 73	1.40
2.68E-05	1148 $\pm$ 25	0.87
1.07E-05	1805 $\pm$ 44	0.55
5.36E-06	2047 $\pm$ 35	0.49
PBS	2507 $\pm$ 45	0.39

[a] The concentration of Gd(III) was corrected by ICP-MS. [b] The longitudinal relaxation  $T_1$  is the average of  $T_1$  values of three slices and SD is the standard deviation, for each sample. [c] The relaxation rate,  $R_1 = 1/T_1$ .

	Size (d.nm...	% Intensity	Width (d.n...
<b>Z-Average (d.nm):</b> 4252	<b>Peak 1:</b> 671.6	100.0	47.98
<b>Pdl:</b> 0.156	<b>Peak 2:</b> 0.000	0.0	0.000
<b>Intercept:</b> 0.577	<b>Peak 3:</b> 0.000	0.0	0.000



**Figure S6.** DLS spectrum of **PtGdL** in aqueous solution. The DLS spectrum of **PtGdL** proves that **PtGdL** could form aggregations in aqueous solution.