Electronic Supplementary Material (ESI) for Chemical Communications

A Hexanuclear Gadolinium-organic Octahedron as a Sensitive MRI Contrast Agent for Selectively Imaging Glucosamine in Aqueous Media

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Contents

1. Experimental

Instruments and reagents All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. ^{1}H NMR spectra was measured on a Varian INOVA 400M spectrometer. ESI mass spectra were carried out on a HPLC-Q-Tof MS spectrometer using methanol as mobile phase. The solution fluorescent spectra and luminescent lifetimes were measured on EDINBURGH FS920. Both excitation and emission slit widths were 5 nm. MR images were performed on MiniMR-20 Imaging & Analyzing system (Shanghai Niumag). The ^{17}O NMR was performed on a Varian INOVA 600M spectrometer

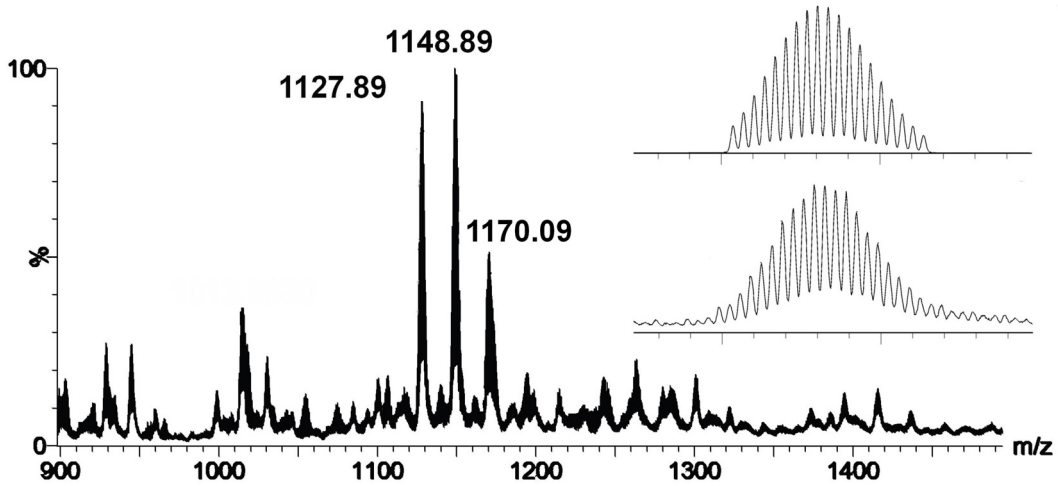
Preparation of Gd-PT1: A solution of $Gd(NO_3)_3{\cdot}6H_2O$ (0.033g, 0.075 mmoL) in methanol (6 mL) was layered onto a solution of **PT1** ligand (0.026g, 0.05mmoL) in $CH_3OH/CHCl_3$ (v:v = 1:4, 6 mL). The solution was left for one week at room temperature to give X-ray quality yellow block crystals. Yield: about 62% (based on the crystals that have been collected and then dried in vacuum).

Crystallography

Intensities data of compound **Gd-PT1** was collected on a BRUKER SMART APEXCCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs. Crystal data for **Gd-PT1**, $C_{116}H_{128}Cl_6Gd_6N_{48}O_{66}$ $[Gd_6(C_{108}H_{78}N_{36}O_{12})(NO_3)_6(H_2O)_6{\cdot}6NO_3{\cdot}2CHCl_3{\cdot}6CH_3OH{\cdot}6H_2O]$, Mr = 4406.86, Rhombohedral, space group *R*-3, *a* = 30.943(1), *c* = 35.509(1) Å, *V* = 29443(1) Å^3, μ = 2.168 mm^{-1}, Z = 6, T = 180 K. 41434 reflections were collected of which 11487 reflections were unique (R_{int} = 0.1457). The final refinement gave R_1 = 0.0795 for 3068 reflections with I ≥ 2σ(I), and wR_2 = 0.2465 for all data.. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL *version* 5.1. Except the solvent molecule, the skeleton non-hydrogen atoms were refined anisotropically and hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. The coordinated nitrates and water molecules on the Gd centers were disordered into two parts with the s.o.f being refined as free variables. For two of the uncoordinated nitrates, the N−O bond distance and the distance between the O atoms were fixed to be same, respectively. Thermal parameters on adjacent atoms in the disordered coordinated nitrates and the two uncoordinated

nitrates were restrained to be similar. Three pyridine rings on the backbone were disordered into two parts with the s.o.f being fixed at 0.5, respectively. For all the disordered rings, the distance between their adjacent C−C and C−N were fixed to be same, thermal parameters on adjacent atoms in the disordered moieties were restrained to be similar.

2. **Figure S1**. ESI-MS spectra f compound Gd-**PT1** in CH_3OH solution. The insert exhibit the measured and the simulated isotopic pattern at 1148.89.



1075.71: $[Gd_6\text{-}(PT1)_4(NO_3)_3(CH_3OH)\text{-}12H]^{3+}$

1099.84: $[Gd_6\text{-}(PT1)_4(NO_3)_3(CH_3OH)(H_2O)_4\text{-}12H]^{3+}$

1185.52: $[Gd_6\text{-}(PT1)_4(NO_3)_7(DMF)(H_2O)_3\text{-}8H]^{3+}$

1194.18: $[Gd_6\text{-}(PT1)_4(NO_3)_8(H_2O)_4\text{-}7H]^{3+}$

1214.87: $[Gd_6\text{-}(PT1)_4(NO_3)_9(H_2O)_4\text{-}6H]^{3+}$

1242.45: $[Gd_6\text{-}(PT1)_4(NO_3)_{10}(DMF)(H_2O)\text{-}5H]^{3+}$

1262.78: $[Gd_6\text{-}(PT1)_4(NO_3)_{11}(H_2O)_5\text{-}4H]^{3+}$

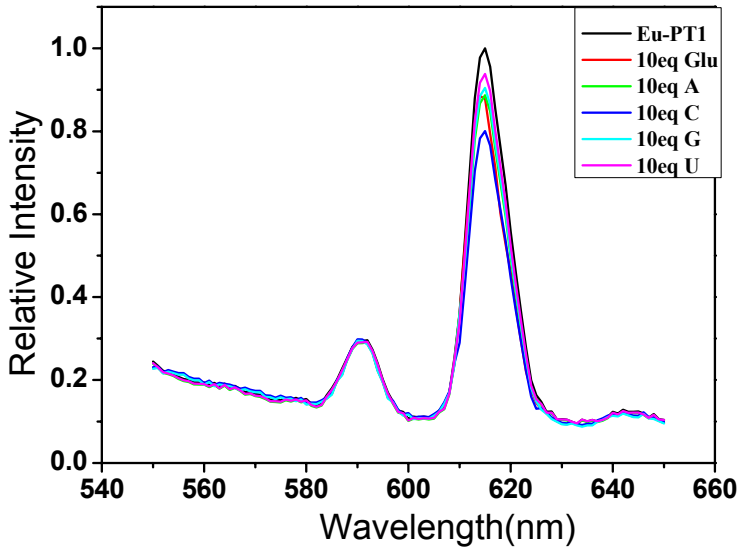
1279.87: $[Gd_6\text{-}(PT1)_4(NO_3)_{11}(CH_3OH)(H_2O)_6\text{-}4H]^{3+}$

1300.88: $[Gd_6\text{-}(PT1)_4(NO_3)_{12}(CH_3OH)(H_2O)_6\text{-}3H]^{3+}$

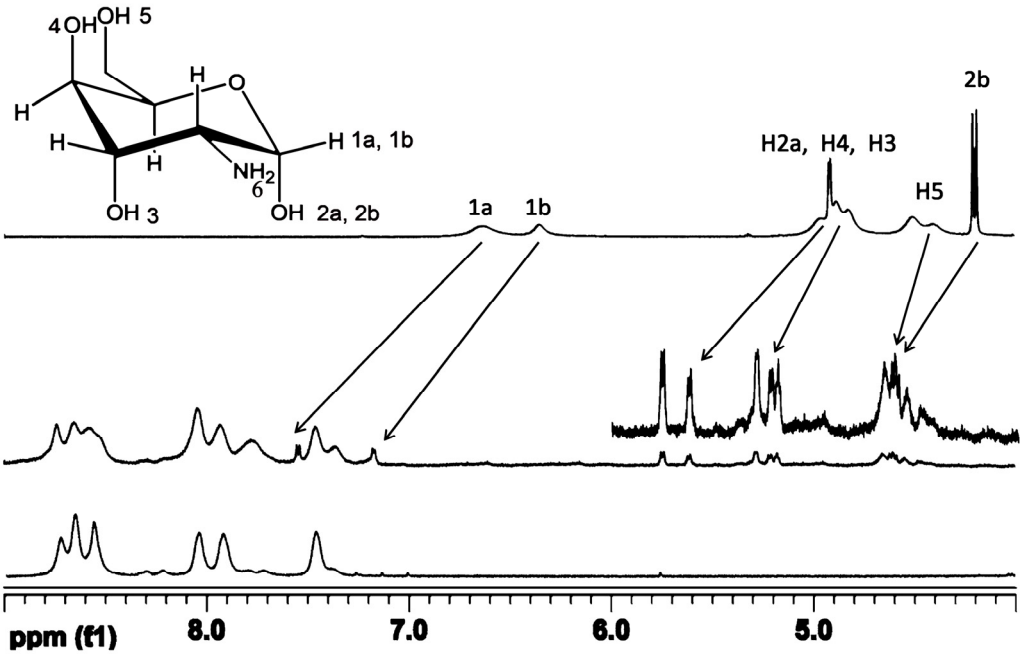
3. **Table S1**. The longitudinal relaxation time T_1 of compound Gd-**PT1**(0.5 mM) in presence of 18 equiv. Glucose (Glu) and RNA-based nucleoside.

	NH_2-Glu	Glu	A	U	C	G
T_1/ms	31.9	5.99	5.57	5.19	6.40	5.53

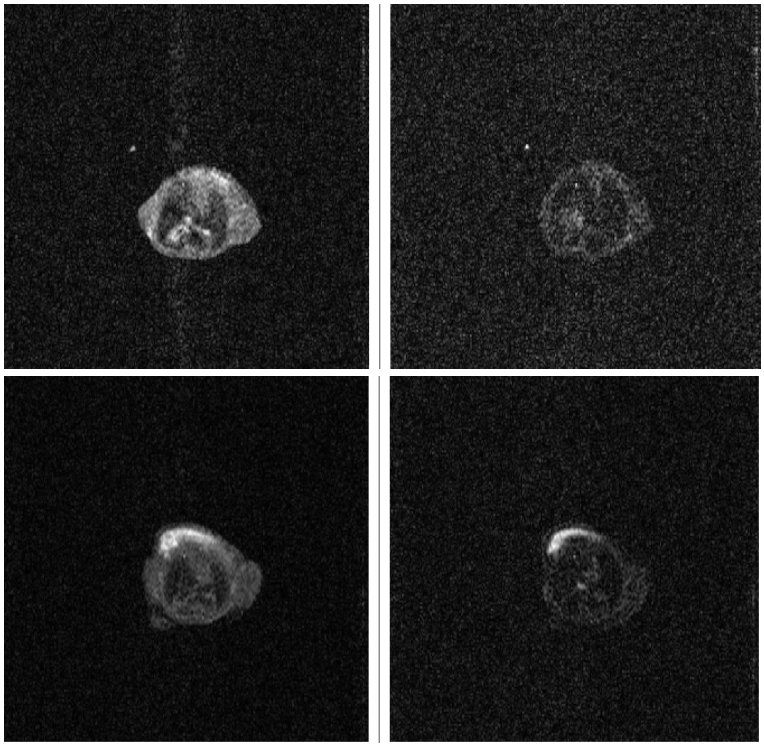
4. Figure S2 The Fluorescence spectrum of Eu-**PT1** upon the addition of 10 equiv. glucose and RNA-based nucleoside.



5. Figure S3. ^{1}H NMR (DMSO-d_6) spectra of Eu-PT1 (bottom); upon addition of 2 equiv. glucosamine (middle); free glucosamine (top)



6. **Figure S4.** MR Transection images of a living mouse hypodermis before (top) and acquired (bottom) injection of Gd-**PT1** (0.5 mM) DMF/H_2O (v/v = 10/1).



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6. **Table S1.** Luminescence Lifetimes (μs) and Calculated Number of Inner-Sphere Water Molecules (q) for Eu-PT1 (0.02 mM) in the Absence and Presence of glucosamine (0.2 mM).

	τ H_2O/μs	τ D_2O/μs	q
Eu-PT1	43.68	47.82	2.08
Eu-PT1 + glucosamine	84.93	93.76	1.03

Luminescence measurements of Eu-PT1 were performed in the absence or presence of excess glucosamine. Samples were excited at 365 nm, and the emission maxium at 615 nm was used to determine luminescence lifetimes. The number of bound water molecules was estimated using Horrocks' equation $q = 1.2(1/\tau_{H2O} - 1/\tau_{D2O} - 0.25)$[1], where τ is the luminescence lifetime in H_2O or D_2O.

Ref : A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. G. Williams and M. Woods, *J. Chem. Soc*., *Perkin Trans. 2*, 1999, 493–503.

7. **Figure S5.** Temperature dependence of ^{17}O NMR traverse relaxation rate of Gd-**PT1** (1mM in DMF/H_2O 7:1 solution)