Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary information for

Gold Nanoparticles Coated with Gadolinium-DTPA-bisamide Conjugate of Penicillamine as a T1-weighted Blood-pool Contrast Agent

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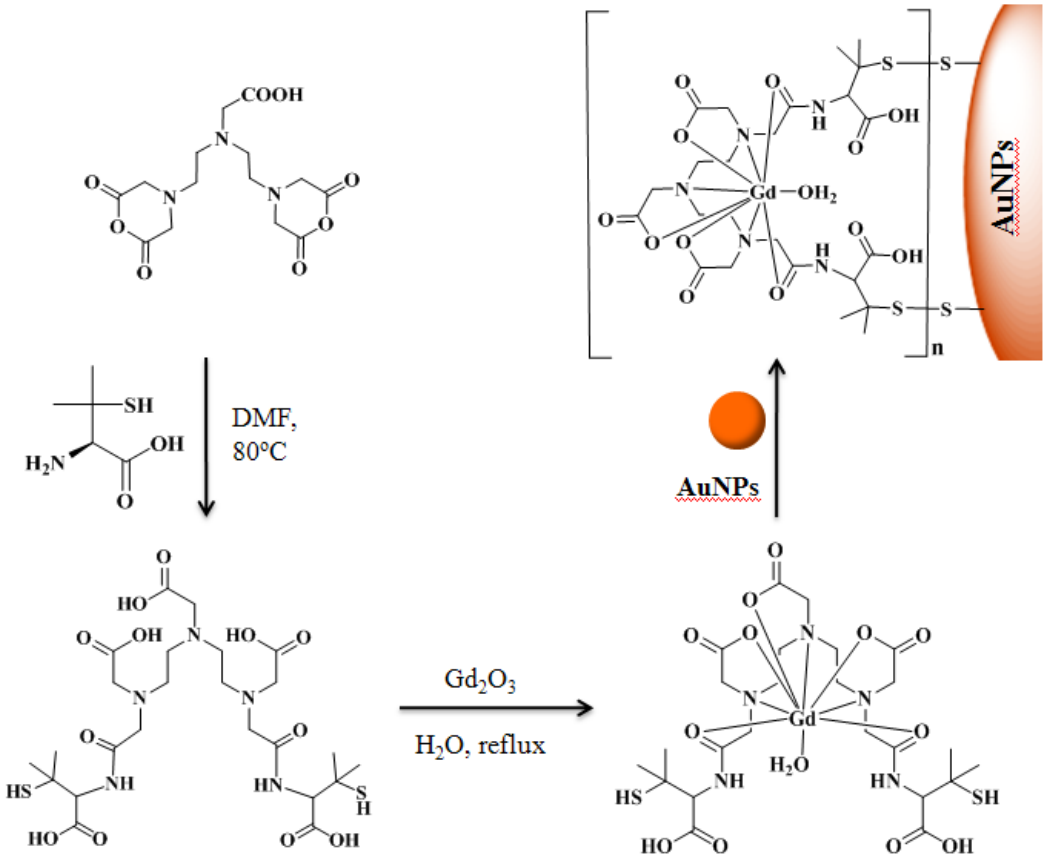
Contents

Scheme 1



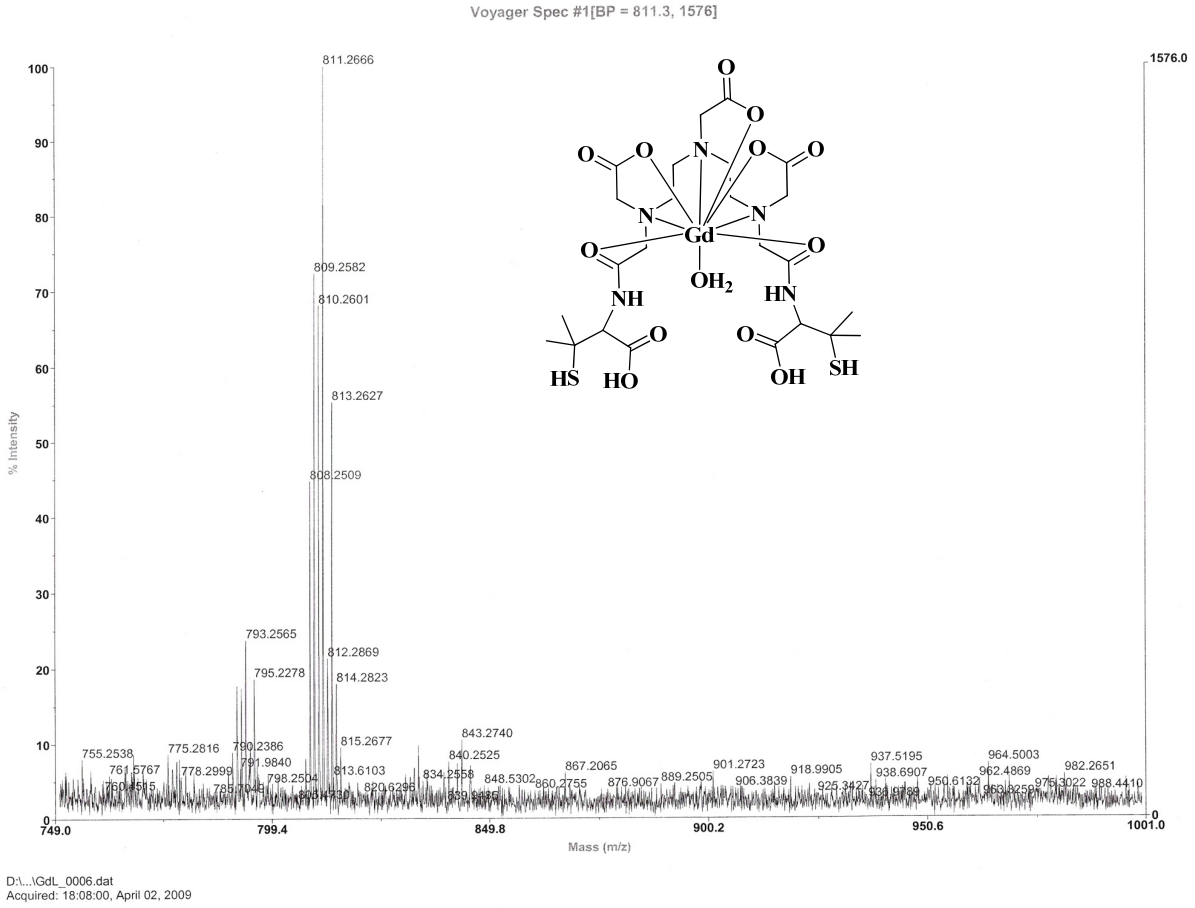


Fig. S1 Maldi-TOF mass spectrum of GdL.

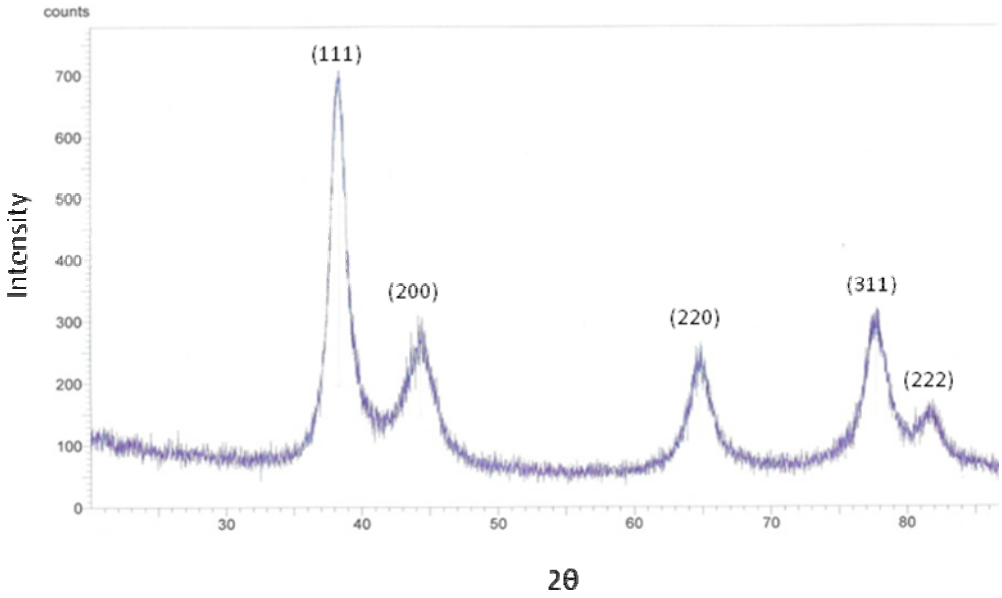


Fig. S2 Powder X-ray diffraction pattern.

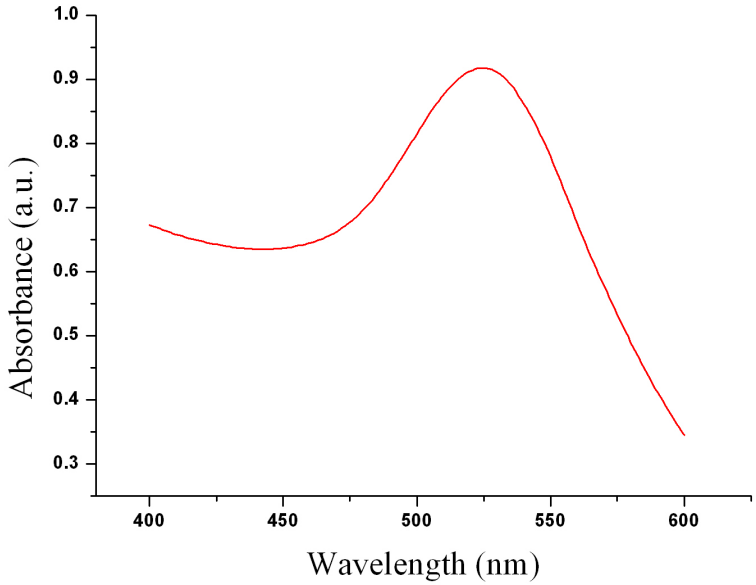


Fig. S3 Visible absorption spectrum of Au@GdL.

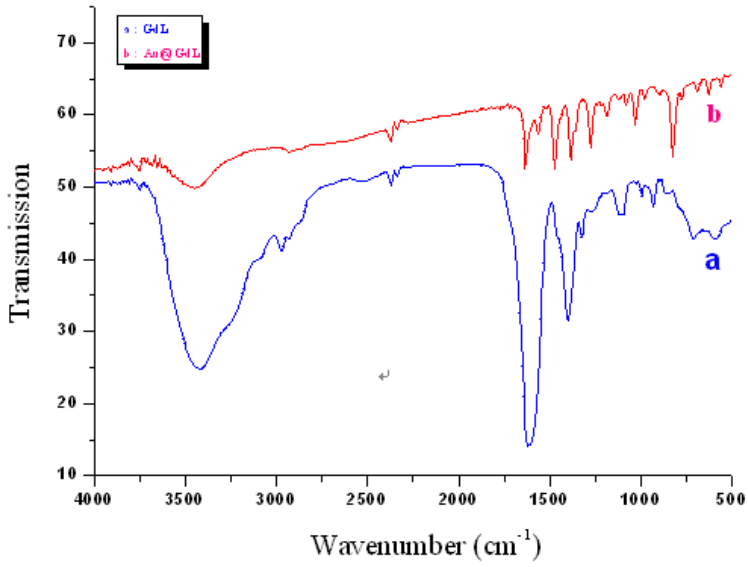


Fig. S4 The FT-IR spectra of (a) GdL and (b) Au@GdL.

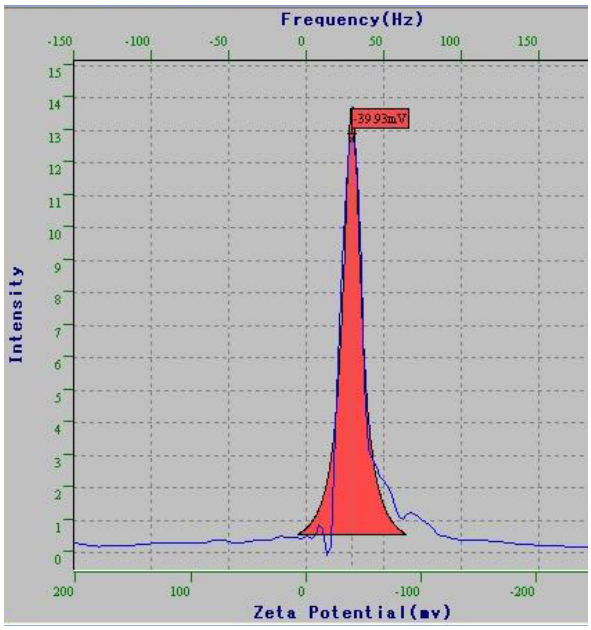


Fig. S5 Zeta potential of Au@GdL.

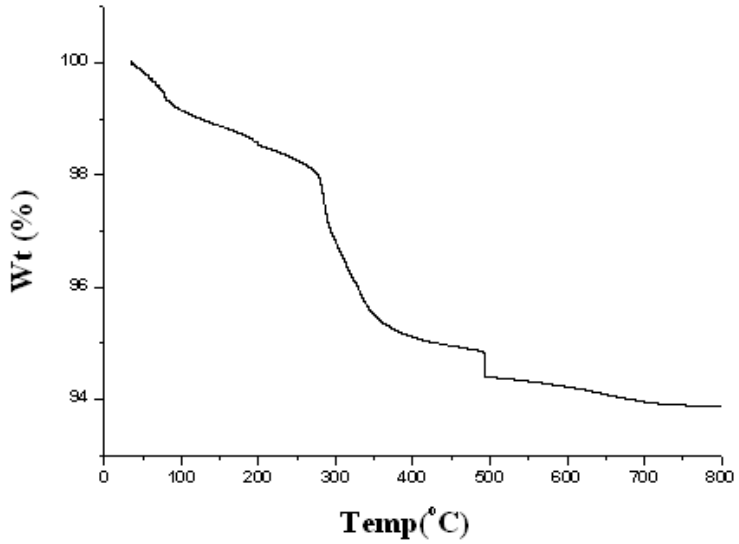


Fig. S6 TGA profile of Au@GdL.

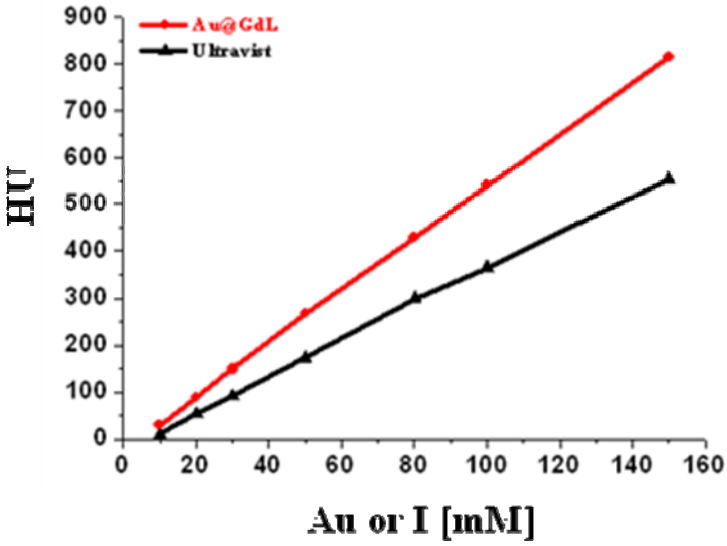


Fig. S7 X-ray attenuation in HU for Au@GdL and Ultravist®.

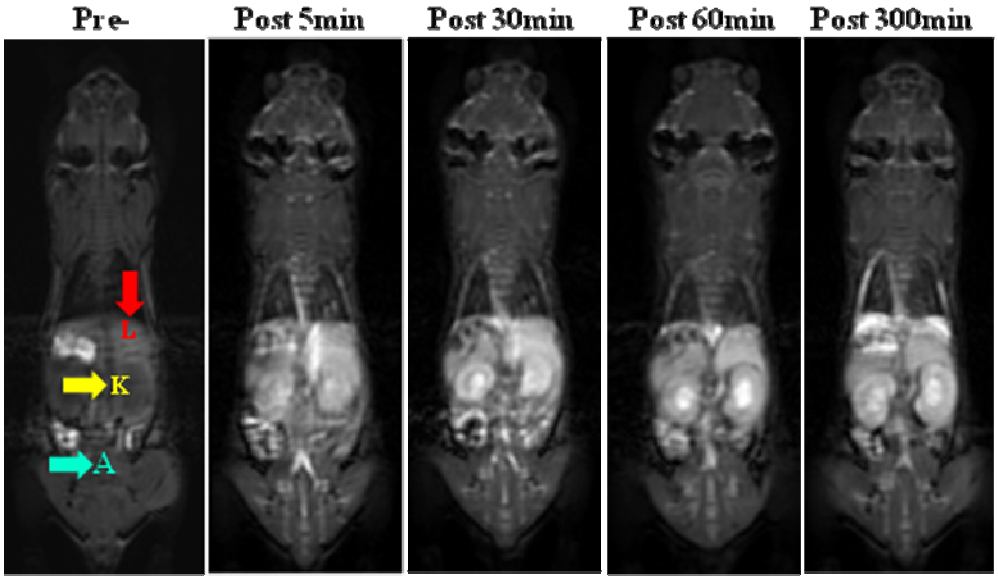


Fig. S8 *In vivo* MR coronal images of mice obtained with Au@GdL (**L**: liver, **K**: kidney, **A**: abdominal aorta).

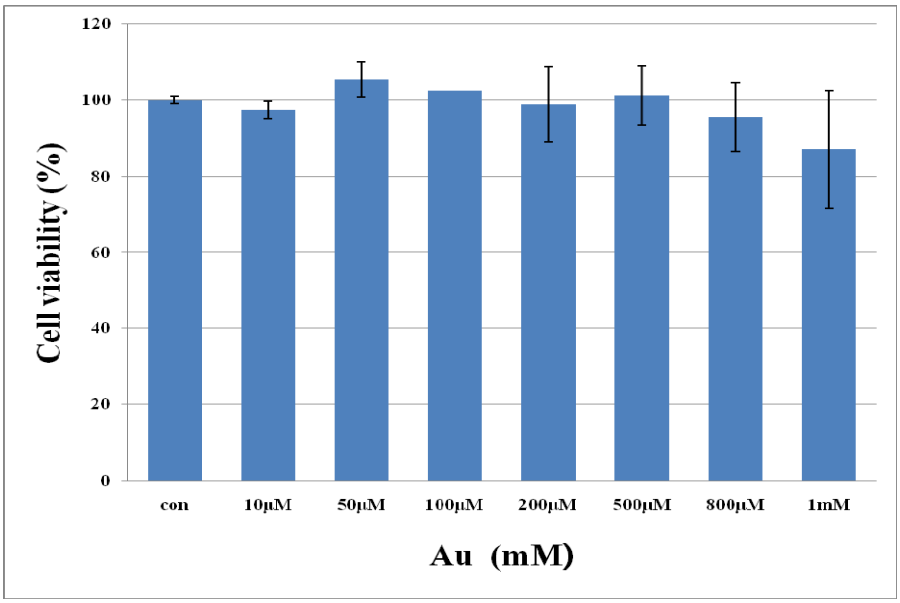


Fig. S9 Cell viability for Au@GdL at various concentrations.

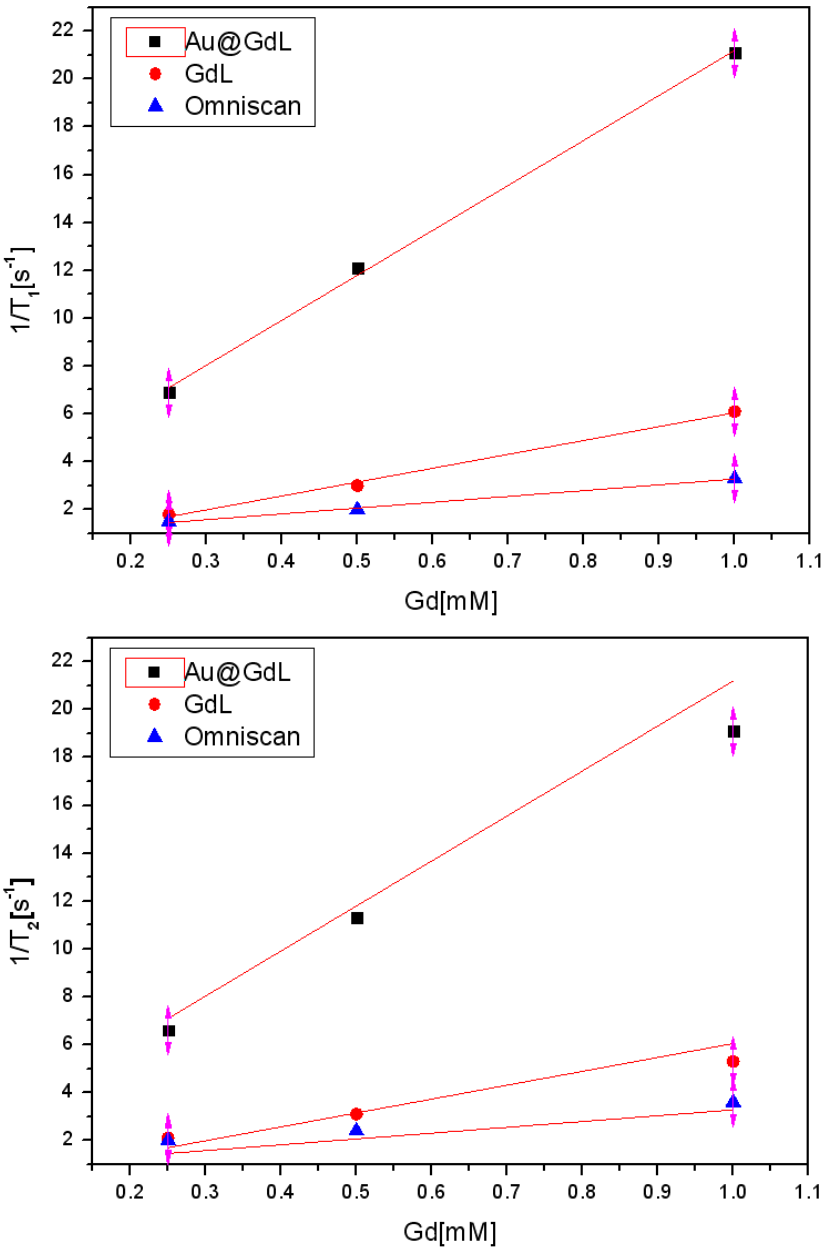


Fig. S10 The relaxivity of Au@GdL, GdL and Omniscan® as a function of [Gd].

Potentiometric Measurements and Computational Method

Potentiometric titrations were performed with an automatic titrator to determine the protonation constants of the DTPA-bis(amide) conjugate of penicillamine (**L**) and the stability constants of Gd (III) complexes. The autotitrating system consists of a 798 MPT Titroprocessor, a 728 stirrer and a PT-100 combination pH electrode (Metrohm). The pH electrode was calibrated using standard buffer solutions. All calibrations and titrations were carried out under a CO_2-free nitrogen atmosphere in a sealed glass vessel (50 cm^3) thermostatted at 25 ± 0.1 °C at an ionic strength of 0.10 mol/dm^3 KCl. The concentrations of the metal-ion and the amide solutions were maintained at approximately 5 mmol/dm^3. A CO_2-free KOH solution (0.100 mol/dm^3) was used as a titrant to minimize the changes in ionic strength during the titration. Dioxygen and carbon dioxide were excluded from the reaction mixtures by maintaining a positive pressure of purified nitrogen in the titration cell. The electromotive force of the cell is given by $E = E'^{o} + Q \log[H^+] + E_j$, and both E'^{o} and Q were determined by titrating a solution with a known hydrogen-ion concentration at the same ionic strength, using the acid range of the titration. The liquid-junction potential (E_j) was found to be negligible under the experimental conditions employed. The protonation constants of the ligands and the stability constants of Gd(III) complexes formed in aqueous solutions were determined from the titration data using the computer program HYPERQUAD.[a] The accuracy of this method was verified by measuring the protonation and the stability constants for Gd(III) complexes of $[DTPA\text{-}BMA]^{3-}$. The results were compared with literature values.[b]

a Gans, A. Sabatini and A. Vacca, *Talanta* 1996, **43**, 1739.

b S. Laurent, T. N. Parac-Vogt, K. Kimpe, C. Thirifays, K. Binnemans, R. N. Muller and L. Vander Elst, *Eur. J. Inorg. Chem.* 2007, **14**, 2061.

Table S1. Protonation constants ($\log K_i^H$) of **L**, stability constants of Gd-complexes of **L** (I = 0.10 mol/dm^3)

Equilibrium	L	DTPA BMA[a]
[HL]/[L][H]	8.04	9.37
$[H_2L]/[HL][H]$	4.82	4.38
$[H_3L]/[H_2L][H]$	2.44	3.31
ΣpK_a	15.30	17.06
[GdL]/[Gd][L]	15.56	16.85
{$\log K_{GdL}$(pH 7.4)}	14.92	14.84

[a]Data obtained from ref.