

Supplementary Information for

Equilibrium and NMR spectroscopic studies on the gadolinium(III), yttrium(III), copper(II) and zinc(II) complexes formed with the DTPA-N,N,N',N''-bis(amide), -bis(n-butylamide) and -bis[bis(n-butylamide)] ligands. Kinetic stabilities of the gadolinium(III) complexes

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- Figure S1** pH dependence of the relaxivities of the Gd³⁺ complexes [(1) GdL², (2) GdL¹, (3) GdL⁰, 25 °C, [GdL] = 1 × 10⁻³ M, 9 MHz]
- Figure S2** ¹H (upper) and ¹³C NMR spectra of YL⁰ complex. The bottom left spectrum shows the CO region while the CH₂ peaks are shown in the bottom right spectrum. T= 323 K, pH = 5.8 and c= 0.05 M in D₂O solution.
- Figure S3.** ¹³C 2D EXSY NMR spectrum of YL⁰ complex. The carbonyl region is shown. T= 323 K, pH = 5.8 and c= 0.05 M in D₂O solution.
- Figure S4** Pseudo-first-order rate constants of the exchange reactions between GdL¹ (5 × 10⁻⁴ M) and Zn²⁺. [Zn²⁺] = 0.03 M (1), 0.02 M (2), 0.015 M (3) and 0.01 M (4) (25 °C, 1.0 M KCl)
- Figure S5.** Pseudo-first-order rate constants of exchange reactions between GdL⁰ (5 × 10⁻⁴ M) and Zn²⁺. [Zn²⁺] = 0.03 M (1), 0.02 M (2), 0.015 M (3) and 0.01 M (4) (25 °C, 1.0 M KCl)
- Figure S6.** Pseudo-first-order rate constants of exchange reactions between GdL¹ (2 × 10⁻⁴ M) and Cu²⁺. [Cu²⁺] = 6 × 10⁻³ M (1), 4 × 10⁻³ M (2), 2 × 10⁻³ M (3) and 1 × 10⁻³ M (4) (25 °C, 1.0 M KCl)
- Figure S7.** Pseudo-first-order rate constants of exchange reactions between GdL² (5 × 10⁻⁴ M) and Zn²⁺. [Zn²⁺] = 0.03 M (1), 0.02 M (2), 0.015 M (3) and 0.01 M (4) (25 °C 1.0 M KCl)
- Figure S8.** Pseudo-first-order rate constants of exchange reactions between GdL² (2 × 10⁻⁴ M) and Cu²⁺. [Cu²⁺] = 6 × 10⁻³ M (1), 4 × 10⁻³ M (2), 2 × 10⁻³ M (3) and 1 × 10⁻³ M (4) (25 °C, 1.0 M KCl)

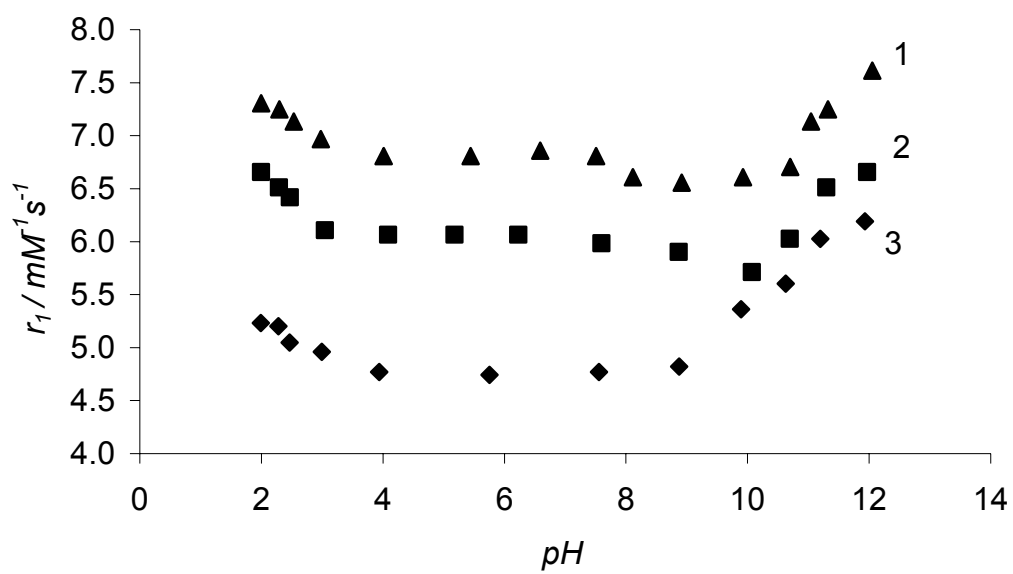


Figure S1 pH dependence of the relaxivities of the Gd³⁺ complexes [(1) GdL², (2) GdL¹, (3) GdL⁰, 25°C, [GdL] = 1×10⁻³ M, 9 MHz]

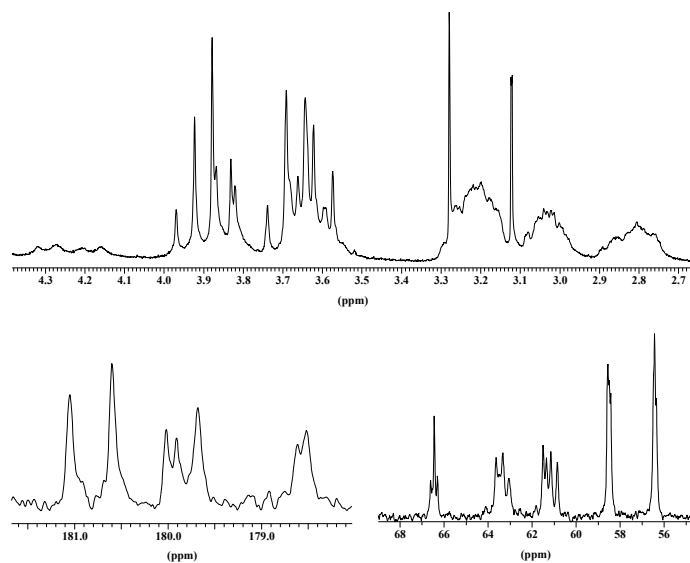


Figure S2 ¹H (upper) and ¹³C NMR spectra of YL⁰ complex. The bottom left spectrum shows the CO region while the CH₂ peaks are shown in the bottom right spectrum. T= 323 K, pH = 5.8 and c= 0.05 M in D₂O solution.

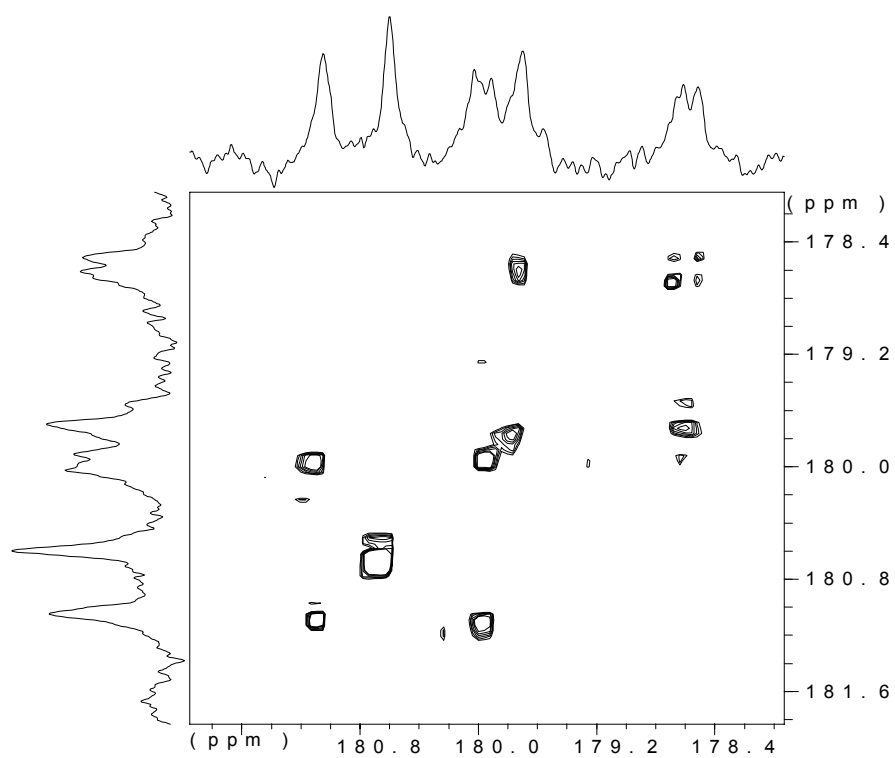


Figure S3. ¹³C 2D EXSY NMR spectrum of YL⁰ complex. The carbonyl region is shown. T= 323 K, pH = 5.8 and c= 0.05 M in D₂O solution.

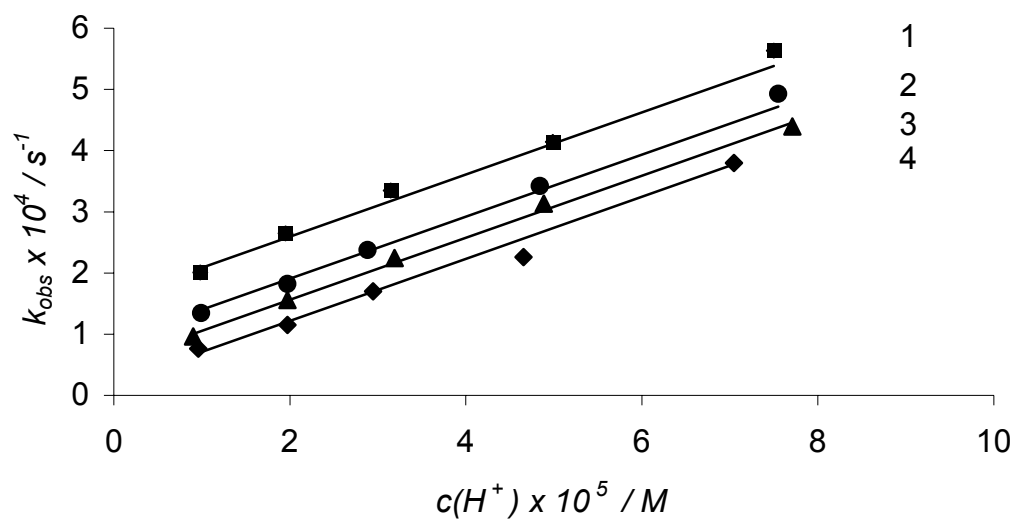


Figure S4 Pseudo-first-order rate constants of the exchange reactions between GdL¹ (5×10^{-4} M) and Zn²⁺. [Zn²⁺] = 0.03 M (1), 0.02 M (2), 0.015 M (3) and 0.01 M (4) (25 °C, 1.0 M KCl)

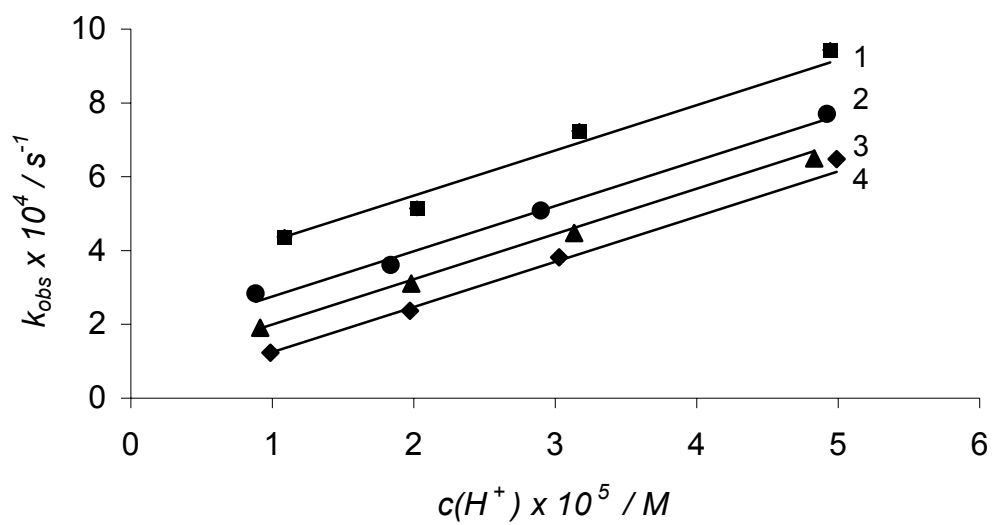


Figure S5. Pseudo-first-order rate constants of exchange reactions between GdL^0 (5×10^{-4} M) and Zn^{2+} . $[Zn^{2+}] = 0.03$ M (1), 0.02 M (2), 0.015 M (3) and 0.01 M (4) (25 °C, 1.0 M KCl)

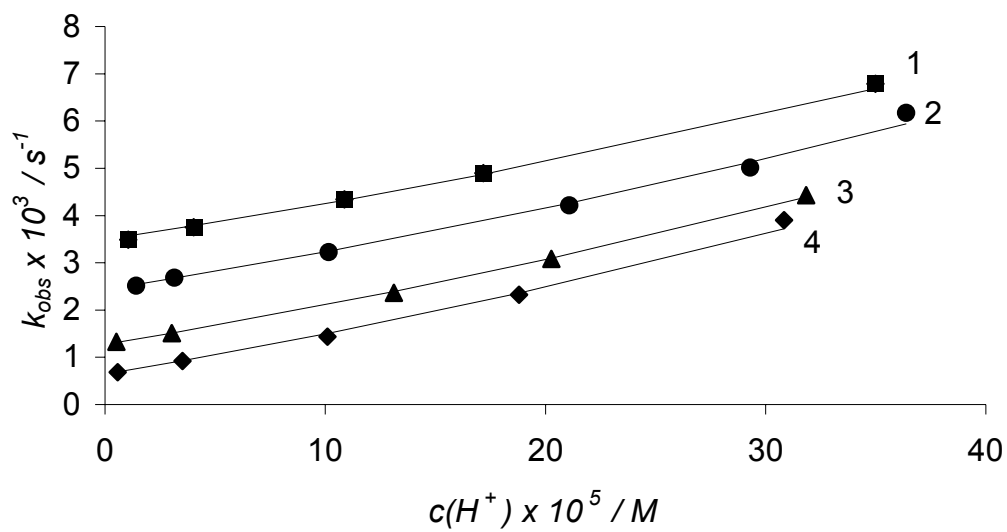


Figure S6. Pseudo-first-order rate constants of exchange reactions between GdL¹ (2×10^{-4} M) and Cu²⁺. [Cu²⁺] = 6×10^{-3} M (1), 4×10^{-3} M (2), 2×10^{-3} M (3) and 1×10^{-3} M (4) (25 °C, 1.0 M KCl)

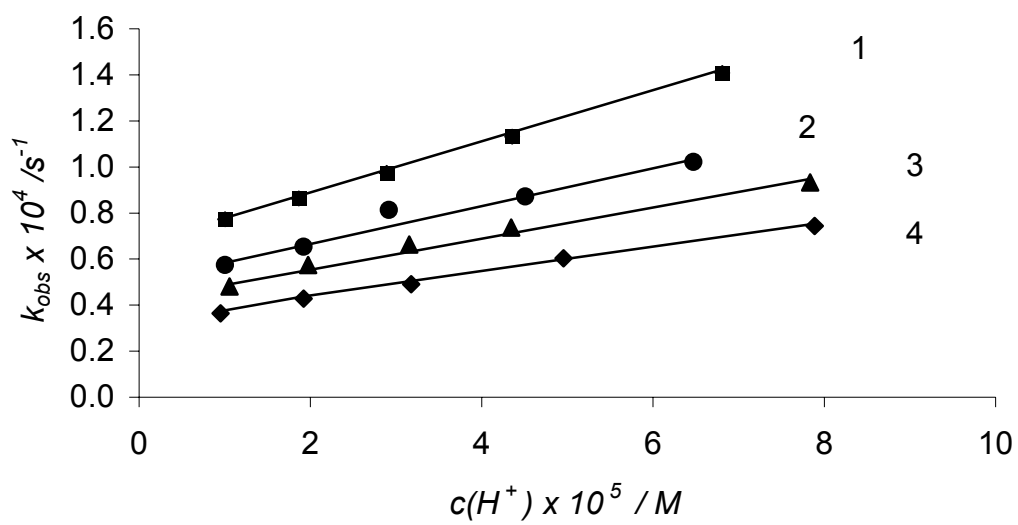


Figure S7. Pseudo-first-order rate constants of exchange reactions between GdL^2 (5×10^{-4} M) and Zn^{2+} . $[Zn^{2+}] = 0.03$ M (1), 0.02 M (2), 0.015 M (3) and 0.01 M (4) (25 °C 1.0 M KCl)

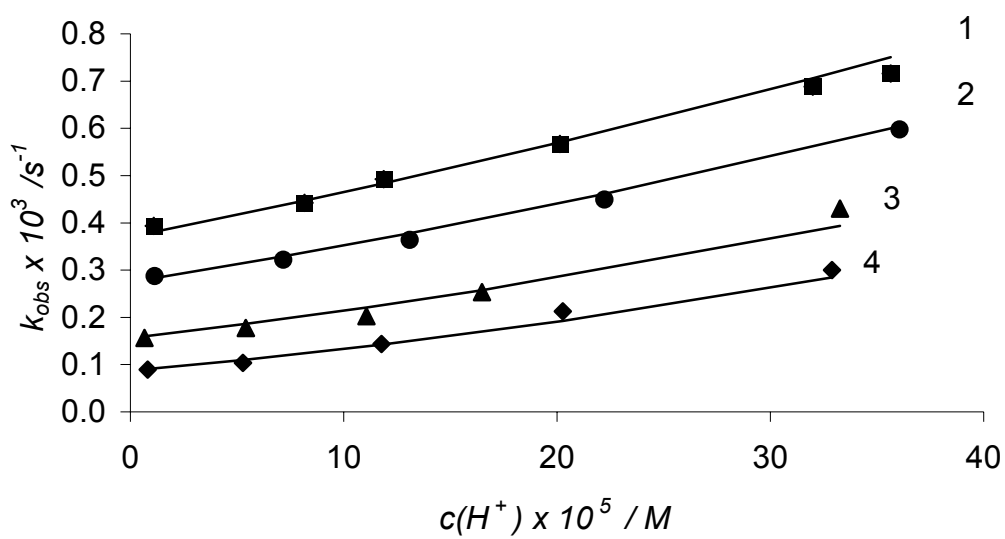


Figure S8. Pseudo-first-order rate constants of exchange reactions between GdL^2 (2×10^{-4} M) and Cu^{2+} . $[Cu^{2+}] = 6 \times 10^{-3}$ M (1), 4×10^{-3} M (2), 2×10^{-3} M (3) and 1×10^{-3} M (4) (25 °C, 1.0 M KCl)