Supplementary Material (ESI) for Chemical Communications

Supplementary materials for:

Lanthanide(III) complexes of a pyridine *N*-oxide analogue of DOTA: exclusive *M* isomer formation induced by six-membered chelate ring

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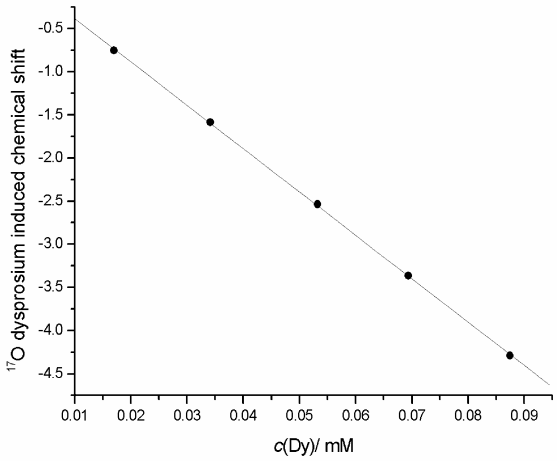

Figure S1. Induced ^{17}O chemical shift of water in presence of [Dy(do3a-pyNox)(H_2O)] (pH = 7, 25 °C, 400 MHz). The slope obtained from least-square was found to be –50.

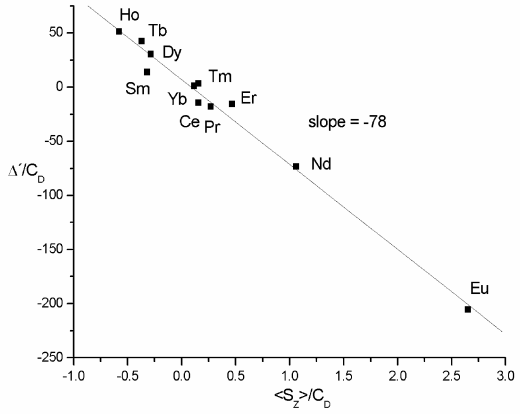

Figure S2A. Water ^{17}O chemical shifts in presence of [Ln(do3a-pyNox)(H_2O)] (pH = 7; 25 °C, 400 MHz).

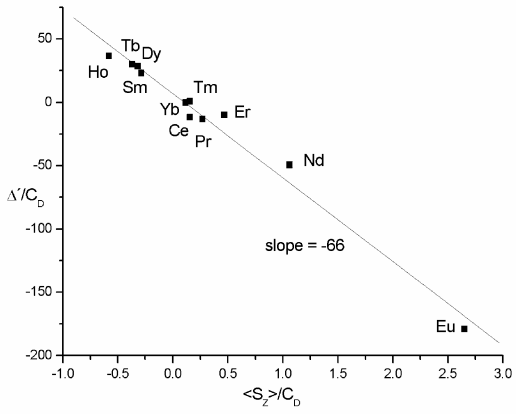

Figure S2B. Water ^{17}O chemical shifts in presence of [Ln(do3a-pyNox)(H_2O)] (pH = 7; 70 °C, 400 MHz).

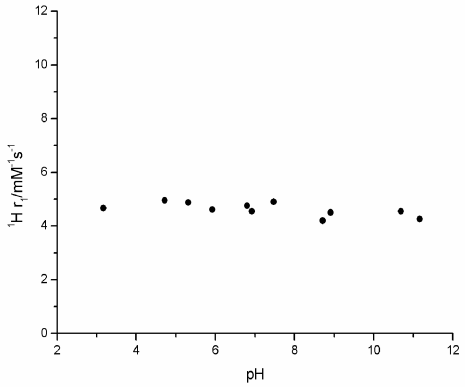

Figure S3. pH dependence of water proton relaxivity in presence of [Gd(do3a-pyNox)(H_2O)] complex.

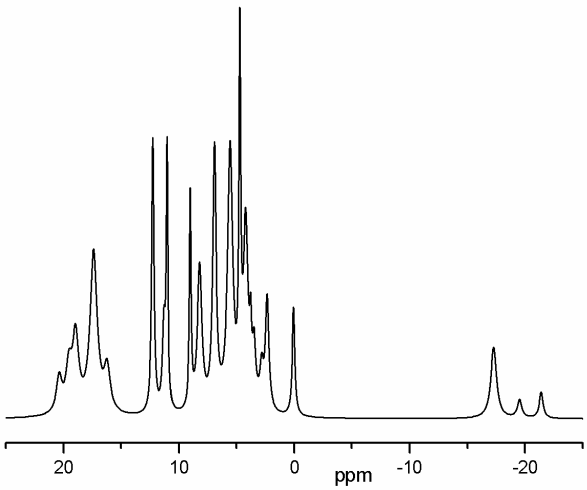

Figure S4A. ^{1}H NMR spectrum of [Nd(do3a-pyNox)(H_2O)] (CD_3OD/D_2O 4/1; 25 °C, 400 MHz).

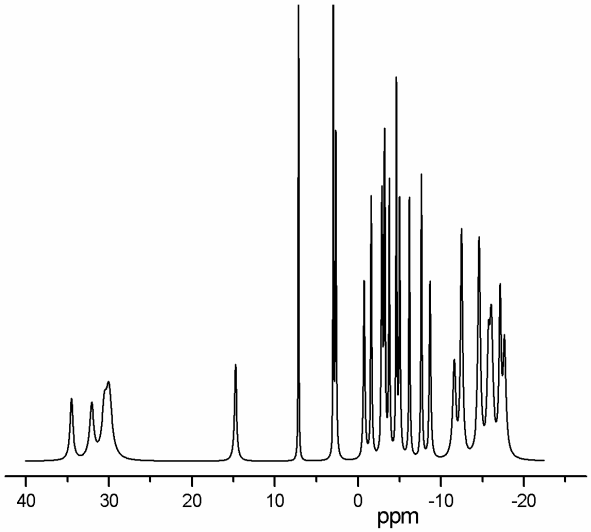

Figure S4B. ^{1}H NMR spectrum of [Eu(do3a-pyNox)(H_2O)] (CD_3OD/D_2O 4/1; 25 °C, 400 MHz).

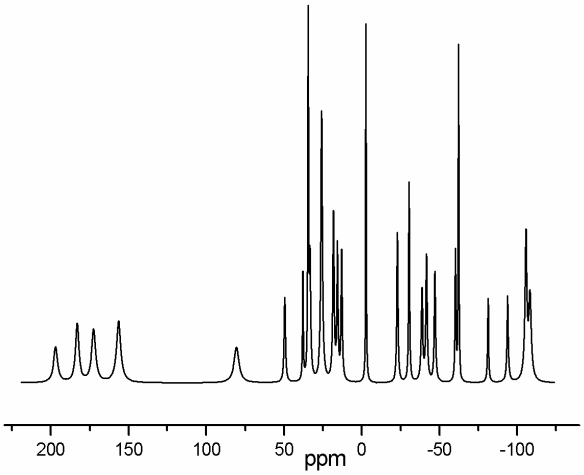

Figure S4C. ^{1}H NMR spectrum of [Yb(do3a-pyNox)(H_2O)] (CD_3OD/D_2O 4/1; –25 °C, 400 MHz).

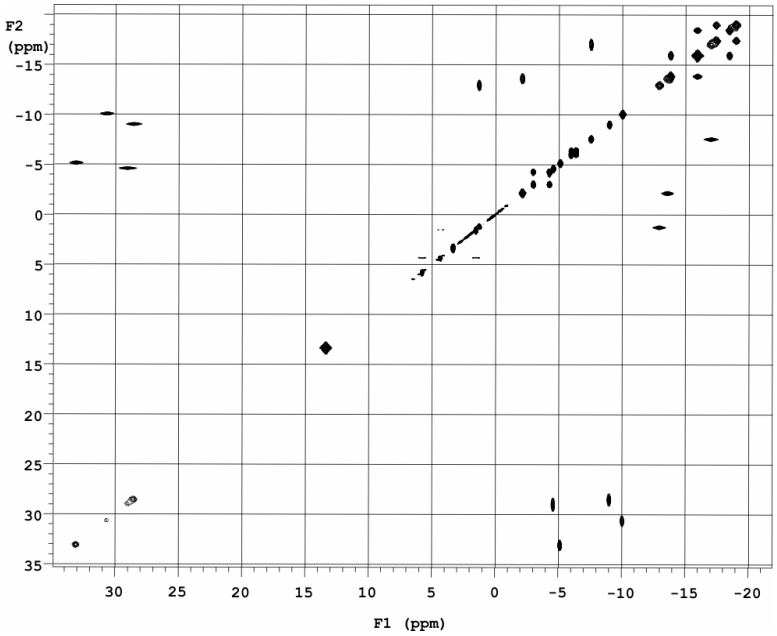

Figure S5. ^{1}H EXSY spectrum of [Eu(do3a-pyNox)(H_2O)] (CD_3OD/D_2O 4/1; 25 °C, 400 MHz). The FID was accumulated 4 h with mixing time t_{mix} = 20 ms.

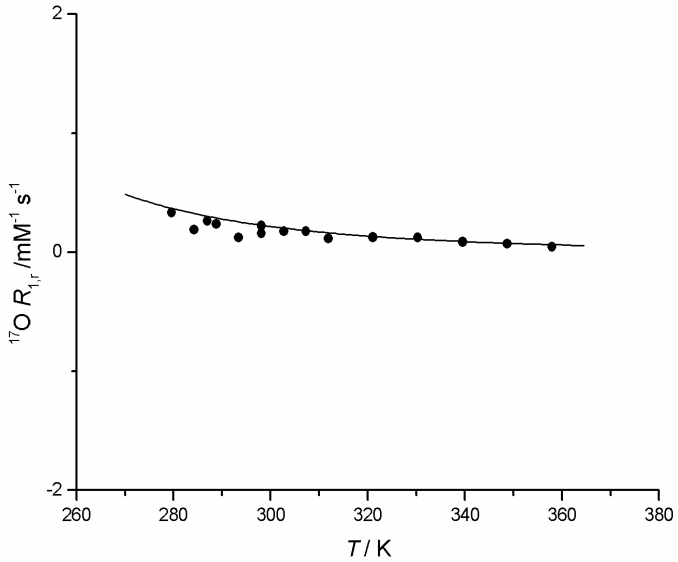

Figure S6A. Variable-temperature water ^{17}O R_{1r} relaxation rates measured in presence of [Gd(do3a-pyNox)(H_2O)] (pH = 7, 400 MHz). The curve represents the best result of simultaneous fitting according to BMS equation.

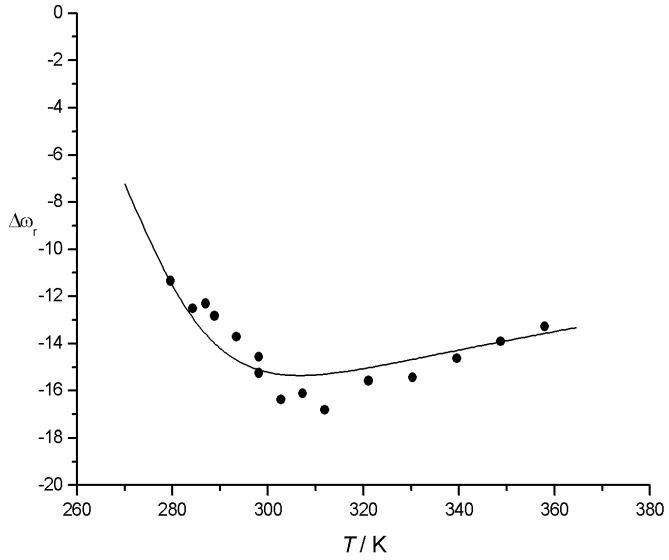

Figure S6B. Variable-temperature water ^{17}O reduced resonance frequences measured in presence of [Gd(do3a-pyNox)(H_2O)] (pH = 7, 400 MHz). The curve represents the best result of simultaneous fitting according to BMS equation.

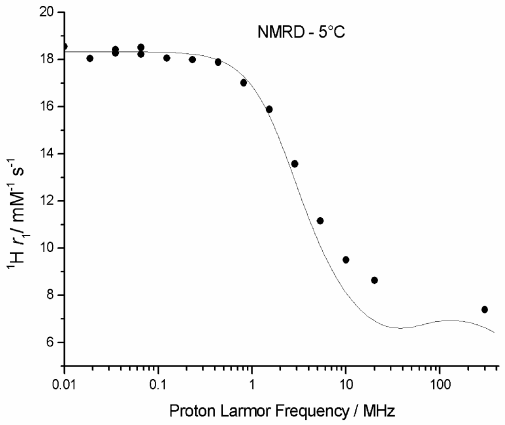

Figure S7A. ^{1}H NMRD profile at pH = 7 and 5 °C. The curve represents the best result of simultaneous fitting according to BSM equations.

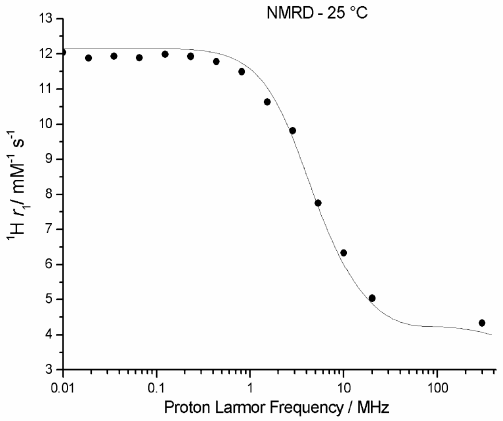

Figure S6B. ^{1}H NMRD profile at pH = 7 and 25 °C. The curve represents the best result of simultaneous fitting according to BMS equations.

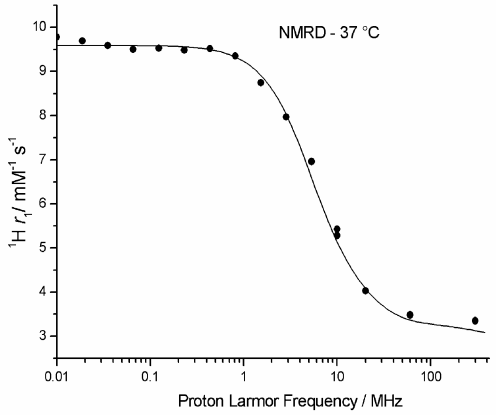

Figure S6C. ^{1}H NMRD profile at pH = 7 and 37 °C. The curve represents the best result of simultaneous fitting according to BSM equations.

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Table S1. The complete set of results obtained from simultaneous least-square fitting of data.

Parameter	[Gd(DO3A-pyNox)(H_2O)]
r_1^{310} [$s^{-1}\cdot mM^{-1}$] [a]	4.04
Δ^2 [10^{20} s^{-2}]	0.69 ± 0.03
τ_M^{298} [ns]	39 ± 1
$\Delta H_M^{\#}$ [$kJ\cdot mol^{-1}$]	51 ± 2
τ_R^{298} [ps]	74 ± 3
τ_v^{298} [ps]	2.7 ± 0.1
$A/\hbar$ [10^6 $rad\cdot s^{-1}$]	-3.75
r_{GdO} [Å]	2.5
r_{GdH} [Å]	3.1
A [Å]	3.5
q	1

[a] The value of milimolar relaxivity was obtained at 37 °C and 20 MHz, the value found for 25 °C and 10 MHz is 6.31 $s^{-1}\cdot mM^{-1}$.