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**Supporting information to:**

**Structures and Dynamics of Ln(III) Complexes of Sugar-Based DTPA-bis(amides) in Aqueous Solution; A Multinuclear NMR Study.**

Hendrik Lammers, Frédéric Maton, Dirk Pubanz, Martijn W. van Laren, Herman van Bekkum, André E. Merbach, Robert N. Muller, and Joop A. Peters

**Table S1**: Measured $^{13}C$ chemical shifts of 0.10 M [Nd(DTPA-bisamide)($H_2O$)] complexes in $D_2O$ at 80 °C and 100.6 MHz.

**Table S2A-C**: Measured longitudinal and transverse relaxation times and chemical shifts of the acidified water reference ($T_{1A}$, $T_{2A}$ and $\Delta\omega_A$) and of the paramagnetic solutions ($T_1$, $T_2$ and $\Delta\omega$), at molar ratios of bound water $P_m$. The calculated values of reduced relaxation rates and chemical shifts ($1/T_{1r}$, $T_{2r}$ and $\Delta\omega_r$) of the variable temperature study on the [Gd(DTPA-bisamide)($H_2O$)] complexes are also tabulated. The variable temperature $^{17}O$ NMR measurements were mainly carried out on a Varian VXR-400 S spectrometer. Several measurements, denoted with an asterisk, were recorded using a Bruker AM-400 spectrometer. All measurements were carried out at 9.4 T.

**Table S3A-C**: Measured transverse relaxation times of the [Gd(DTPA-bisamide)($H_2O$)] complexes ($T_2$) and of the acidified water (0.9 m perchloric acid) reference ($1/T_{2A}$) and the calculated reduced relaxation rates ($1/T_{2r}$) at variable pressure. The reduced relaxation times were calculated taking into account an activation volume of +1.09 $cm^3mol^{-1}$ for the reference. The measurements were recorded on a Bruker AM-400 spectrometer at 9.4 T.

**Table S4**: Comparison of water exchange rates at temperature T, $k_{ex}^T$ (VT) as calculated from eq 17 using the parameters obtained from the variable temperature data, with the corresponding water exchange rates at zero pressure and temperature T, $k_0^T$ (VP), as obtained from simultaneous least squares fits of the variable pressure data using eqs 8, 12, 15, 19, 21, 22 and 27.

**Table S5A-C**: Longitudinal proton relaxation rates ($T_1$) for the [Gd(DTPA-bisamide)(H2O)] complexes at several temperatures T. The data at 0.01 MHz to 50 MHz were obtained on an IBM Research Relaxometer using the field cycling method. The spin-lattic proton relaxation rates at 200 MHz and 400 MHz were measured on a Bruker MSL-200 spectrometer and a Varian VXR-400 S spectrometer, respectively.

**Figure S1**: NMRD profiles for the complexes [Gd(DTPA-BPDA)($H_2O$)], [Gd(DTPA-BGLUCA)($H_2O$)] and [Gd(DTPA-BENGALAA)($H_2O$)]. The curves are calculated with the parameters obtained from the simultaneous least-squres fittings (see text). The bottom lines in each box represent the outer sphere contribution to the relaxivity.

**Table S1.**

| Assign. | DTPA-BEA | DTPA-BPDA | DTPA-BLUCA | DTPA-BENGALAA | DTPA-BPA[a] |
|---|---|---|---|---|---|
| *C*=O | 186.54 | 186.54 | 187.04 | 187.15 | 186.38 |
| | 182.75 | 183.32 | 183.23 | 183.04 | 182.95 |
| | 180.18 | 176.55 | 176.46 | 177.65 | 177.04 |
| | 178.97 | 173.48 | 174.70 | 176.01 | 175.99 |
| | 172.78 | 171.24 | 171.35 | 173.54 | 172.68 |
| | 170.56 | 168.29 | 168.07 | 170.70 | 170.84 |
| | 167.70 | 164.63 | 164.06 | 167.48 | 168.07 |
| | 164.04 | | | | 164.70 |
| $CH_2COOH$ | 70.20 | 67.55 | 67.69 | 62.39 | 70.67 |
| | 66.78 | 62.58 | 66.15 | 57.44 | 67.24 |
| | 65.26 | 60.56 | 63.17 | 55.79 | 61.18 |
| | 62.70 | 56.62 | 60.64 | | 55.57 |
| | 55.23 | | 59.28 | | |
| | | | 56.22 | | |
| | | | 55.31 | | |
| $N^1CH_2CH_2N^3$ | 32.52 | 33.31 | 32.62 | 32.35 | 33.11 |
| $N^1CH_2CH_2N^3$ | 24.09 | 25.34 | 24.29 | 24.08 | 25.08 |
| *C*-α (*C*-β) | | | | 40.11 (1)[b] (48.37) | |
| | | | | 39.32 (3) (46.70) | |
| | | | | 37.78 (3) (46.49) | |
| | | | | 36.79 (1) (46.22) | |
| *C*-1 | 44.88 (1)[b] | 45.48 (2)[b] | 45.64 (4)[b] | 52.41 | 45.02 (Propyl) |
| | 44.45 (2) | 45.00 (2) | 45.11 (2) | 51.33 | 44.47 (Propyl) |
| | 43.81 (2) | 43.81 (2) | 44.93 (2) | | 43.37 (Propyl) |
| | 42.25 (1) | 43.06 (1) | 44.10 (2) | | 42.58 (Propyl) |
| | | | 43.94 (2) | | |
| | | | 43.46 (1) | | |
| | | | 43.24 (1) | | |
| | | | 43.04 (1) | | |

[a] reference 20; [b] ratio of the signal intensities

**Table S2A**. [Gd(DTPA-BPDA)($H_2O$)] $P_m$ = 2.79 $10^{-3}$

| T (K) | $10^3$K (T) | $T_{1A}$ (s) | $T_1$ (s) | ln($1/T_{1r}$) | $T_{2A}$ (s) | $T_2$ (s) | ln($1/T_{2r}$) | $\nu_A$ ($s^{-1}$) | $\nu$ ($s^{-1}$) | $\Delta\omega_r$ (rad $s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 271* | 3.69 | | | | 2.85E-03 | 1.84E-03 | 11.15 | 720 | 690 | -6.78E+04 |
| 283 | 3.53 | 4.45E-03 | 2.90E-03 | 10.67 | 4.09E-03 | 1.76E-03 | 11.66 | 208 | 201 | -1.58E+04 |
| 302 | 3.31 | 7.76E-03 | 4.76E-03 | 10.28 | 6.17E-03 | 7.69E-04 | 12.92 | 161 | 153 | -1.80E+04 |
| 321 | 3.12 | 1.13E-02 | 7.51E-03 | 9.68 | 8.38E-03 | 3.25E-04 | 13.87 | 117 | 71 | -1.04E+04 |
| 323 | 3.10 | 1.19E-02 | 7.89E-03 | 9.64 | 8.71E-03 | 3.54E-04 | 13.79 | 602 | 530 | -1.62E+05 |
| 338 | 2.96 | 1.65E-02 | 1.08E-02 | 9.35 | 9.02E-03 | 2.36E-04 | 14.21 | 69 | -114 | -4.12E+05 |
| 358 | 2.79 | 2.24E-02 | 1.42E-02 | 9.13 | 1.44E-02 | 2.50E-04 | 14.16 | 24 | -195 | -4.93E+05 |
| 375 | 2.67 | 2.72E-02 | 1.86E-02 | 8.17 | 1.47E-02 | 3.27E-04 | 13.75 | -21 | -302 | -6.33E+05 |

**Table S2B**. [Gd(DTPA-GLUCA)($H_2O$)] $P_m$ = 3.44 $10^{-3}$

| T (K) | $10^3$K (T) | $T_{1A}$ (s) | $T_1$ (s) | ln($1/T_{1r}$) | $T_{2A}$ (s) | $T_2$ (s) | ln($1/T_{2r}$) | $\nu_A$ ($s^{-1}$) | $\nu$ ($s^{-1}$) | $\Delta\omega_r$ (rad $s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 270* | 3.70 | | | | | | | 720 | 702 | -3.29E+04 |
| 273* | 3.67 | | | | | | | 710 | 686 | -4.38E+04 |
| 283 | 3.53 | 4.29E-03 | 2.37E-03 | 10.92 | 3.95E-03 | 1.35E-03 | 11.87 | | | |
| 287* | 3.49 | | | | | | | 701 | 694 | -1.28E+04 |
| 302 | 3.31 | 7.82E-03 | 3.62E-03 | 10.67 | 6.03E-03 | 5.62E-04 | 13.06 | | | |
| 322 | 3.11 | 1.20E-02 | 5.87E-03 | 10.13 | 7.81E-03 | 2.35E-04 | 14.00 | | | |
| 324* | 3.09 | 1.19E-02 | 5.99E-03 | 10.09 | | | | 603 | 494 | -1.99E+05 |
| 341 | 2.93 | 1.57E-02 | 8.58E-03 | 9.64 | 9.33E-03 | 1.73E-04 | 14.32 | 82 | -57 | -2.54E+05 |
| 360 | 2.78 | 2.23E-02 | 1.20E-02 | 9.32 | 1.11E-02 | 2.00E-04 | 14.17 | 42 | -233 | -5.02E+05 |
| 374 | 2.67 | 2.67E-02 | 1.48E-02 | 9.08 | 1.32E-02 | 2.64E-04 | 13.89 | 76 | -257 | -6.08E+05 |
| 393 | 2.54 | 3.34E-02 | 1.89E-02 | 8.80 | 1.23E-02 | 4.53E-04 | 13.33 | -47 | -304 | -4.69E+05 |

**Table S2C.** [Gd(DTPA-BENGALAA)($H_2O$)] $P_m$ = 3.68 $10^{-3}$

| T (K) | $10^3$K (T) | $T_{1A}$ (s) | $T_1$ (s) | ln($1/T_{1r}$) | $T_{2A}$ (s) | $T_2$ (s) | ln($1/T_{2r}$) | $\nu_A$ ($s^{-1}$) | $\nu$ ($s^{-1}$) | $\Delta\omega_r$ (rad $s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 273* | 3.67 | | | | | | | -1584 | -1619 | -5.98E+04 |
| 279 | 3.59 | 3.73E-03 | 2.12E-03 | 10.92 | 3.67E-03 | 1.81E-03 | 11.24 | | | |
| 287* | 3.49 | | | | | | | -1590 | -1615 | -4.27E+04 |
| 288 | 3.47 | 5.09E-03 | 2.54E-03 | 10.89 | 4.48E-03 | 1.70E-03 | 11.50 | | | |
| 297 | 3.36 | 6.68E-03 | 3.03E-03 | 10.80 | 5.16E-03 | 1.26E-03 | 12.00 | | | |
| 311* | 3.22 | | | | | | | -1601 | -1625 | -4.10E+04 |
| 312 | 3.21 | 9.28E-03 | 4.08E-03 | 10.53 | 6.20E-03 | 6.16E-04 | 12.89 | | | |
| 314* | 3.19 | | | | | | | -1613 | -1638 | -4.27E+04 |
| 323* | 3.10 | | | | | | | -1620 | -1669 | -8.37E+04 |
| 326 | 3.07 | 1.19E-02 | 5.26E-03 | 10.27 | 7.43E-03 | 3.05E-04 | 13.66 | | | |
| 340 | 2.94 | 1.68E-02 | 7.04E-03 | 10.02 | 8.45E-03 | 2.08E-04 | 14.06 | 48 | -9 | -9.61E+04 |
| 359 | 2.79 | 2.23E-02 | 9.66E-03 | 9.68 | 6.86E-03 | 1.94E-04 | 14.12 | 2 | -182 | -3.15E+05 |
| 368 | 2.72 | 2.53E-02 | 1.07E-02 | 9.59 | 1.32E-02 | 2.09E-04 | 14.06 | -21 | -315 | -5.03E+05 |
| 377 | 2.65 | 2.76E-02 | 1.18E-02 | 9.48 | 9.12E-03 | 2.30E-04 | 13.96 | -38 | -344 | -5.23E+05 |
| 391 | 2.56 | 3.46E-02 | 1.57E-02 | 9.15 | 5.83E-03 | 3.33E-04 | 13.55 | -70 | -310 | -4.09E+05 |

**Table S3A**. [Gd(DTPA-BPDA)($H_2O$)] $P_m = 2.79\ 10^{-3}$ T = 302.6 K

| *P* (MPa) | $T_2$ (s) | $T_{2A}$ (s) | $1/T_{2r}$ (s-1) | $\ln(1/T_{2r})$ |
|---|---|---|---|---|
| 0.60 | 6.95E-04 | 8.46E-03 | 4.73E+05 | 13.07 |
| 4.00 | 7.17E-04 | 8.48E-03 | 4.58E+05 | 13.03 |
| 25.00 | 7.63E-04 | 8.55E-03 | 4.28E+05 | 12.97 |
| 50.00 | 7.96E-04 | 8.65E-03 | 4.09E+05 | 12.92 |
| 75.00 | 8.59E-04 | 8.74E-03 | 3.76E+05 | 12.84 |
| 101.00 | 8.90E-04 | 8.84E-03 | 3.62E+05 | 12.80 |
| 124.00 | 9.32E-04 | 8.93E-03 | 3.45E+05 | 12.75 |
| 152.00 | 1.01E-03 | 9.04E-03 | 3.16E+05 | 12.66 |
| 172.50 | 1.06E-03 | 9.12E-03 | 2.99E+05 | 12.61 |
| 201.20 | 1.12E-03 | 9.23E-03 | 2.81E+05 | 12.55 |

**Table S3B**. [Gd(DTPA-BGLUCA)($H_2O$)] $P_m = 3.44\ 10^{-3}$ T = 302.5 K

| *P* (MPa) | $T_2$ (s) | $T_{2A}$ (s) | $1/T_{2r}$ (s-1) | $\ln(1/T_{2r})$ |
|---|---|---|---|---|
| 0.60 | 5.30E-04 | 8.44E-03 | 5.14E+05 | 13.15 |
| 4.00 | 5.30E-04 | 8.46E-03 | 5.14E+05 | 13.15 |
| 26.00 | 5.73E-04 | 8.54E-03 | 4.73E+05 | 13.07 |
| 51.50 | 6.12E-04 | 8.63E-03 | 4.41E+05 | 13.00 |
| 78.00 | 6.51E-04 | 8.73E-03 | 4.13E+05 | 12.93 |
| 99.00 | 6.78E-04 | 8.81E-03 | 3.96E+05 | 12.89 |
| 126.00 | 7.19E-04 | 8.92E-03 | 3.72E+05 | 12.83 |
| 151.00 | 7.46E-04 | 9.01E-03 | 3.57E+05 | 12.79 |
| 173.00 | 8.08E-04 | 9.10E-03 | 3.28E+05 | 12.70 |
| 198.00 | 8.38E-04 | 9.20E-03 | 3.15E+05 | 12.66 |

**Table S3C**. [Gd(DTPA-BENGALAA)($H_2O$)] $P_m = 3.67\ 10^{-3}$ T = 311.9 K

| *P* (MPa) | $T_2$ (s) | $T_{2A}$ (s) | $1/T_{2r}$ (s-1) | $\ln(1/T_{2r})$ |
|---|---|---|---|---|
| 0.60 | 5.86E-04 | 1.04E-02 | 4.39E+05 | 12.99 |
| 0.60 | 6.00E-04 | 1.04E-02 | 4.28E+05 | 12.97 |
| 28.00 | 6.30E-04 | 1.05E-02 | 4.07E+05 | 12.92 |
| 50.00 | 6.56E-04 | 1.07E-02 | 3.90E+05 | 12.87 |
| 77.00 | 7.03E-04 | 1.08E-02 | 3.62E+05 | 12.80 |
| 100.00 | 7.19E-04 | 1.09E-02 | 3.54E+05 | 12.78 |
| 127.00 | 7.68E-04 | 1.10E-02 | 3.30E+05 | 12.71 |
| 150.00 | 7.81E-04 | 1.11E-02 | 3.24E+05 | 12.69 |
| 174.50 | 8.36E-04 | 1.12E-02 | 3.02E+05 | 12.62 |
| 201.00 | 8.52E-04 | 1.14E-02 | 2.96E+05 | 12.60 |

**Table S4.**

| Complex | $T$ (K) | $k_{ex}^{T}$ (VT)[a] ($10^5 s^{-1}$) | $k_0^{T}$ (VP)[b] ($10^5 s^{-1}$) |
|---|---|---|---|
| $[Gd(DTPA\text{-}BPDA)(H_20)]$ | 302.6 | 4.7 | 5.1 |
| $[Gd(DTPA\text{-}BGLUCA)(H_2O)]$ | 302.5 | 5.1 | 5.7 |
| $[Gd(DTPA\text{-}BENGALAA)(H_2O)]$ | 311.9 | 4.9 | 4.8 |

[a] values obtained by calculation from eq 17.

[b] exchange rate at zero pressure and temperature $T$.

**Table S5A.** [Gd(DTPA-BPDA)($H_2O$)] c = 1mM pH = 7.37

| $\omega_I$ (MHz) | $T_1$ (s) | | | | |
|---|---|---|---|---|---|
| | 5 °C | 15 °C | 25 °C | 37 °C | 45 °C |
| 0.01 | 6.397 | 5.994 | 6.344 | 6.472 | 6.313 |
| 0.02 | 6.428 | 5.832 | 6.356 | 6.528 | 6.263 |
| 0.04 | 6.393 | 5.971 | 6.157 | 6.489 | 6.265 |
| 0.100 | 6.478 | 5.929 | 6.227 | 6.552 | 6.364 |
| 0.200 | 6.357 | 5.904 | 6.248 | 6.591 | 6.246 |
| 0.400 | 6.329 | 5.930 | 6.233 | 6.455 | 6.417 |
| 1.000 | 6.338 | 5.791 | 6.202 | 6.390 | 6.271 |
| 2.000 | 5.908 | 5.712 | 6.055 | 6.199 | 6.013 |
| 4.000 | 5.600 | 5.359 | 5.710 | 5.812 | 5.741 |
| 10.000 | 4.825 | 4.524 | 4.967 | 4.828 | 4.616 |
| 20.000 | 4.541 | 3.949 | 4.432 | 4.373 | 3.857 |
| 30.000 | 4.133 | 4.020 | 4.198 | 3.938 | 3.539 |
| 200.00 | 3.915 | 3.824 | 3.893 | 3.800 | 3.436 |
| 400.00 | 3.582 | 3.576 | 4.002 | 3.687 | 3.286 |

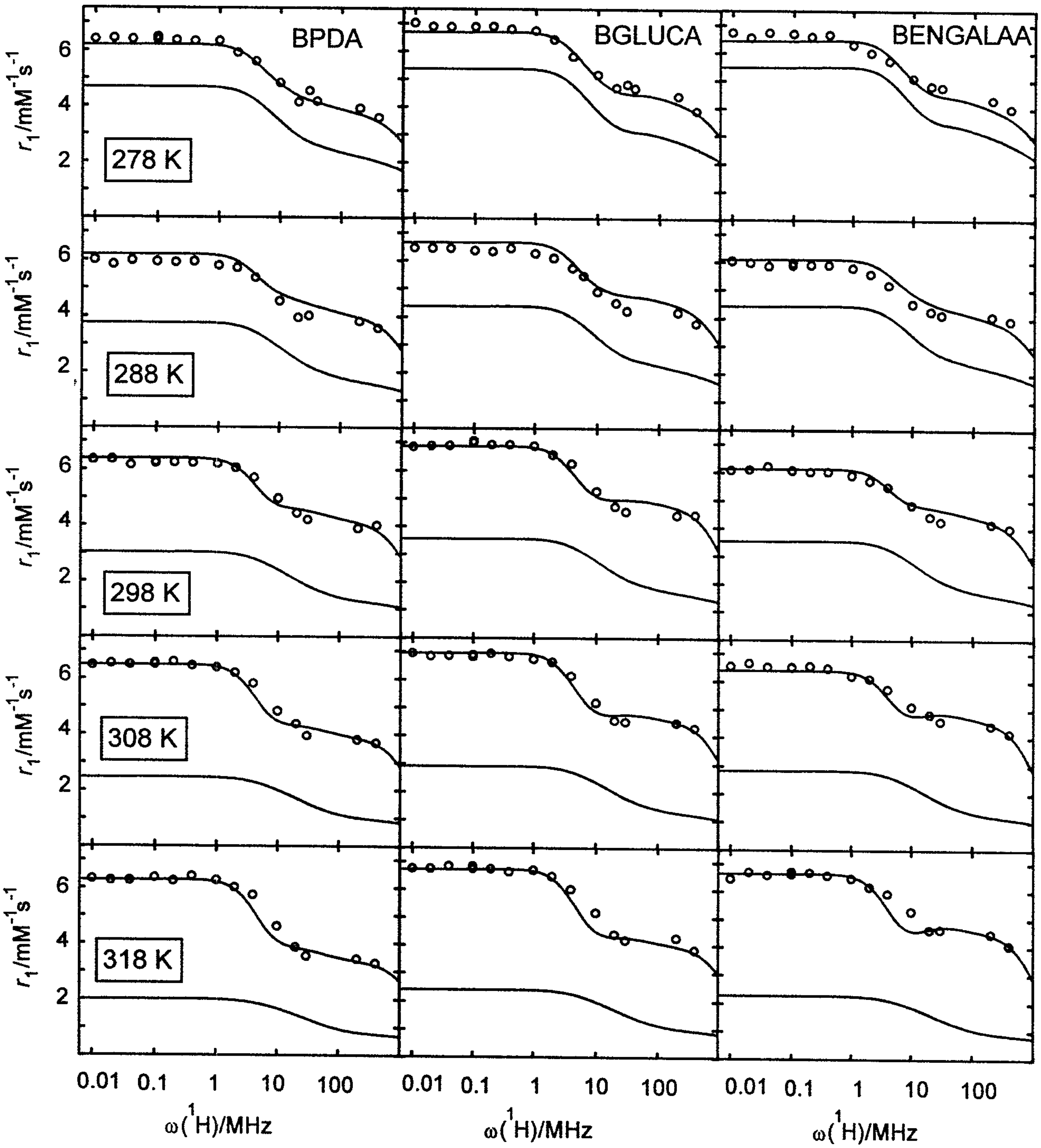
**Table S5B.** [Gd(DTPA-BGLUCA)($H_2O$)] c = 1mM pH = 7.35

| $\omega_I$ (MHz) | $T_1$ (s) | | | | |
|---|---|---|---|---|---|
| | 5 °C | 15 °C | 25 °C | 37 °C | 45 °C |
| 0.01 | 7.012 | 6.438 | 6.839 | 6.949 | 6.753 |
| 0.02 | 6.886 | 6.434 | 6.879 | 6.846 | 6.755 |
| 0.04 | 6.879 | 6.429 | 6.890 | 6.865 | 6.847 |
| 0.100 | 6.882 | 6.357 | 7.005 | 6.832 | 6.755 |
| 0.200 | 6.896 | 6.321 | 6.922 | 6.948 | 6.745 |
| 0.400 | 6.805 | 6.432 | 6.923 | 6.829 | 6.644 |
| 1.000 | 6.746 | 6.250 | 6.880 | 6.741 | 6.705 |
| 2.000 | 6.429 | 6.092 | 6.570 | 6.640 | 6.479 |
| 4.000 | 5.820 | 5.740 | 6.262 | 6.152 | 6.018 |
| 10.000 | 5.169 | 4.892 | 5.275 | 5.189 | 5.175 |
| 20.000 | 4.705 | 4.498 | 4.724 | 4.563 | 4.396 |
| 30.000 | 4.826 | 4.226 | 4.544 | 4.517 | 4.187 |
| 200.00 | 4.398 | 4.180 | 4.412 | 4.479 | 4.268 |
| 400.00 | 3.869 | 3.787 | 4.430 | 4.293 | 3.834 |

**Table S5C.** [Gd(DTPA-BENGALAA)($H_2O$)] c = 1mM pH = 6.88

| $\omega_1$ (MHz) | $T_1$ (s) | | | | |
|---|---|---|---|---|---|
| | 5 °C | 15 °C | 25 °C | 37 °C | 45 °C |
| 0.01 | 6.727 | 6.041 | 6.088 | 6.558 | 6.462 |
| 0.02 | 6.547 | 5.977 | 6.115 | 6.661 | 6.699 |
| 0.04 | 6.729 | 5.861 | 6.235 | 6.534 | 6.596 |
| 0.100 | 6.694 | 5.978 | 6.092 | 6.515 | 6.714 |
| 0.200 | 6.590 | 5.908 | 6.038 | 6.564 | 6.689 |
| 0.400 | 6.663 | 5.903 | 6.041 | 6.489 | 6.585 |
| 1.000 | 6.300 | 5.803 | 5.917 | 6.216 | 6.488 |
| 2.000 | 6.013 | 5.585 | 5.718 | 6.114 | 6.181 |
| 4.000 | 5.726 | 5.182 | 5.503 | 5.744 | 5.938 |
| 10.000 | 5.102 | 4.523 | 4.857 | 5.126 | 5.300 |
| 20.000 | 4.822 | 4.264 | 4.437 | 4.856 | 4.638 |
| 30.000 | 4.769 | 4.143 | 4.264 | 4.611 | 4.652 |
| 200.00 | 4.316 | 4.088 | 4.176 | 4.449 | 4.496 |
| 400.00 | 4.003 | 3.929 | 4.017 | 4.170 | 4.077 |

**Figure S1**


BPDA
BGLUCA
BENGALAA
278 K
288 K
298 K
308 K
318 K
$r_1$/mM$^{-1}$s$^{-1}$
6
4
2
0.01
0.1
1
10
100
ω($^1$H)/MHz