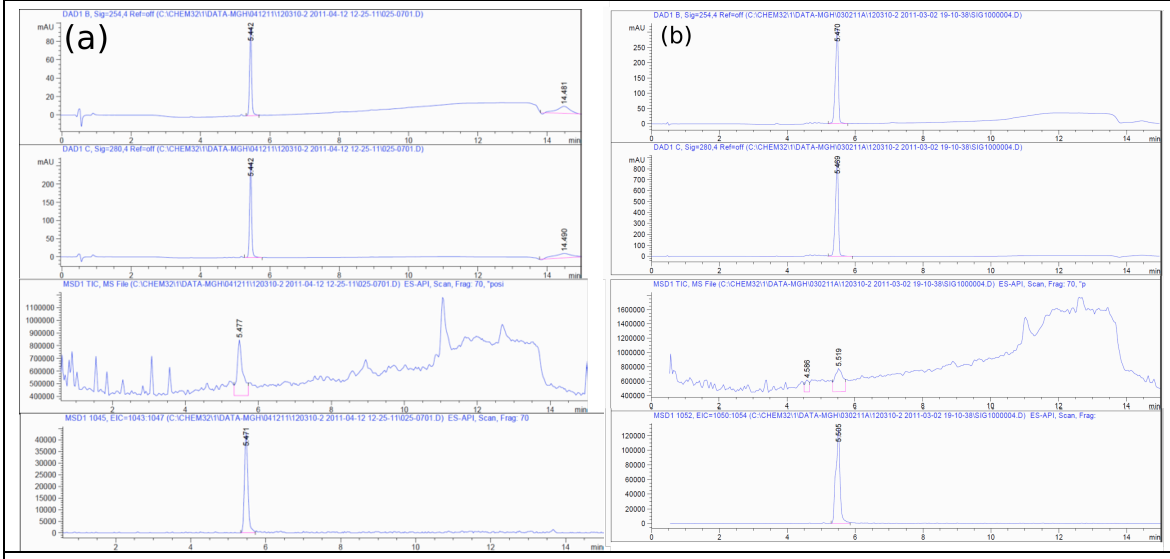
Figure S1: Complexes analyzed by LC-MS, from top to bottom: UV traces (254 nm and 280 nm), total ion current and extracted ion of (a) **Eu-bbu**, (b) **Gd-bbu** and (c) **Gd-glu.** Purity higher than 99.0% in each case.



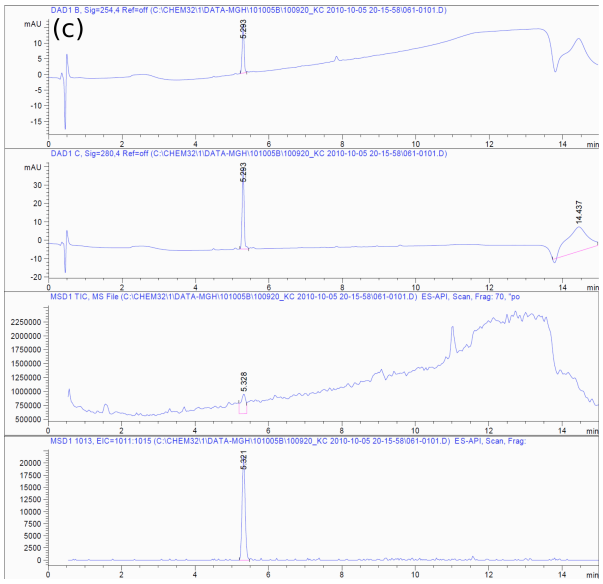
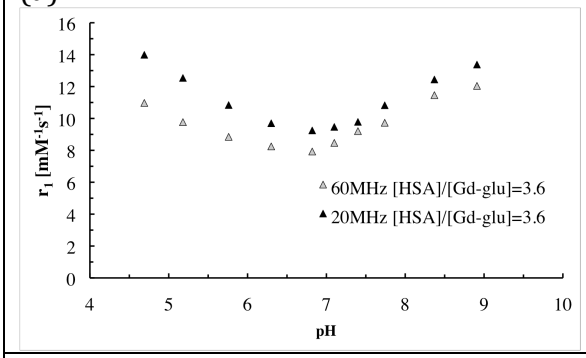
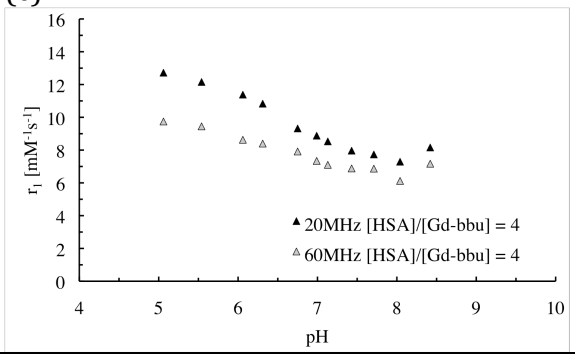


Figure S2: relaxivity r_1 [$mM^{-1}s^{-1}$] at 37°C of (a) **Gd-glu** with HSA (ratio [HSA]/[**Gd-glu**]=3.6, grey triangle=60 MHz, black triangle=20MHz), (b) **Gd-glu** without HSA (grey circle=60 MHz, black circle=20MHz), (c) **Gd-bbu** with HSA (ratio [HSA]/[**Gd-bbu**]=3.3, grey triangle=60 MHz, black triangle=20MHz) and (d) **Gd-bbu** without HSA (grey circle=60 MHz, black circle=20MHz).

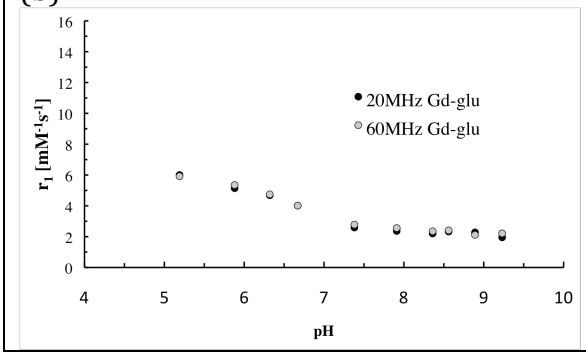
(a)



(c)



(b)



(d)

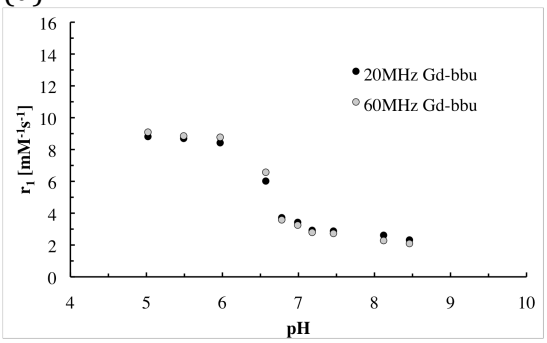
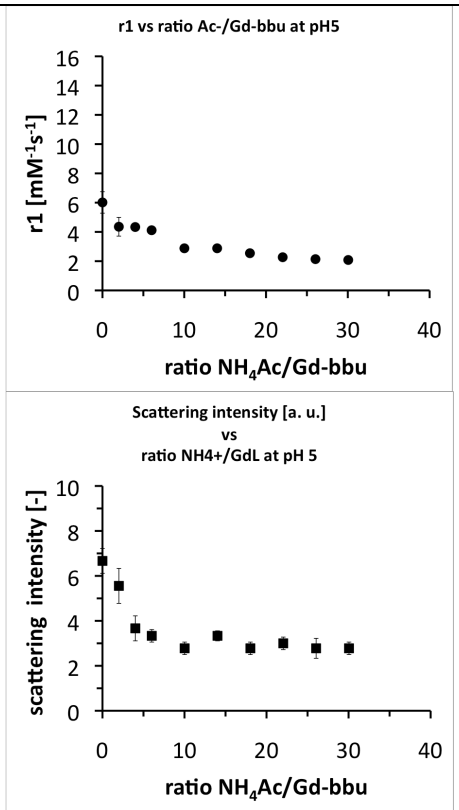


Figure S3

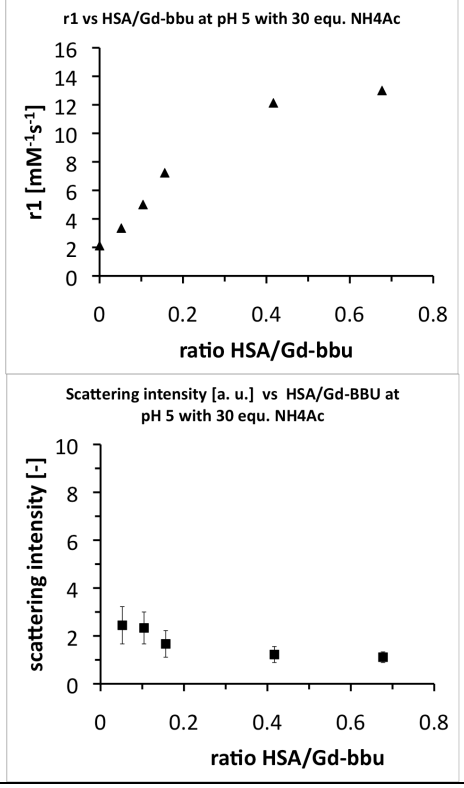
(a) relaxivity r_1 [$mM^{-1}s^{-1}$] at 37°C and 20 MHz (upper figure) and relative scattering intensity (lower figure, relative scattering intensity; a values of 1 = no aggregation) of **Gd-bbu** vs ratio [ammonium acetate]/[**Gd-bbu**] in absence of HSA (0.22 mM Gd(III)) at pH 5.0.

At pH 5, the addition of ammonium acetate decreases the relaxivity and scattering intensity but the results suggest that aggregation is still present but the aggregate is in a different form.



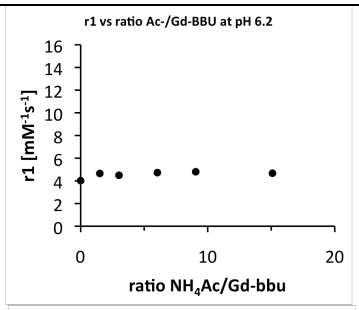
(b) relaxivity r_1 [$mM^{-1}s^{-1}$] at 37°C and 20 MHz (upper figure) and relative scattering intensity (lower figure) of **Gd-bbu** vs ratio [HSA]/[**Gd-bbu**] (0.20 mM Gd(III)) with 30 equivalent of ammonium acetate at pH 5.0.

At pH 5, in the presence of 30 equivalent of ammonium acetate, the addition of HSA increases the relaxivity to the value that would be observed without ammonium acetate. The relative scattering intensity decreases indicating that the addition of HSA to the solution containing 30 eq of ammonium acetate breaks up the aggregate of **Gd-bbu**.



(c) relaxivity r_1 [$mM^{-1}s^{-1}$] at 37°C and 20 MHz (upper figure) and relative scattering intensity (lower figure) of **Gd-bbu** vs ratio [ammonium acetate]/[**Gd-bbu**] in absence of HSA (0.20 mM Gd(III)) at pH 6.2.

At pH 6.2, the addition of 30 equivalents of NH_4OAc has no effect on relaxivity. This result is consistent with the work of Lowe et al. who found that the presence of acetate did not reduce the relaxivity of their complexes. DLS data show no indication of aggregation



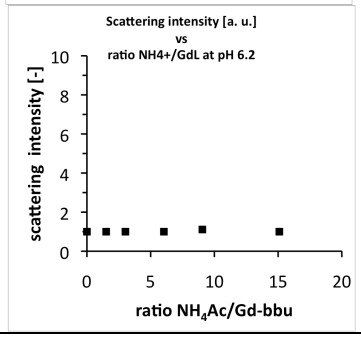
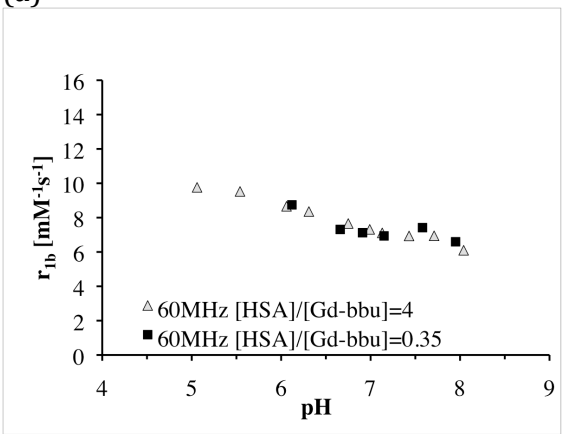


Figure S4: bound relaxivities (r_1^{bd}) of **Gd-bbu** bound to HSA at (a) 60 MHz and (b) 20 MHz and 37°C with a ratio [HSA]/[**Gd-bbu**] = 4 and 0.35. Data indicates that bound relaxivity is constant at each binding site.

(a)



(b)

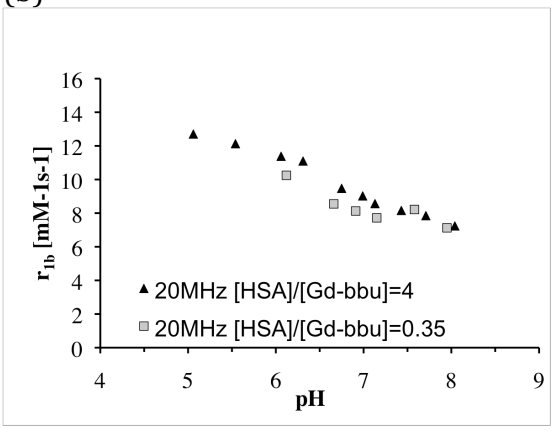
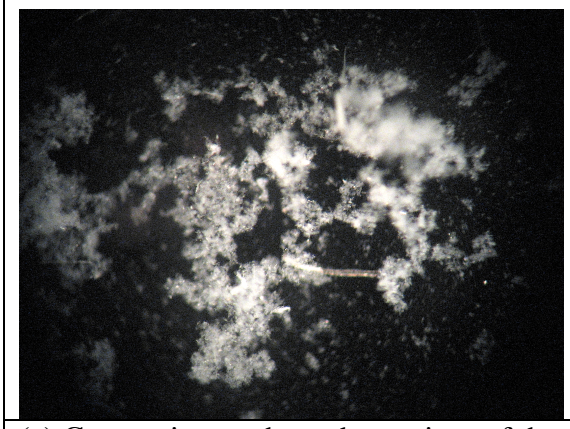
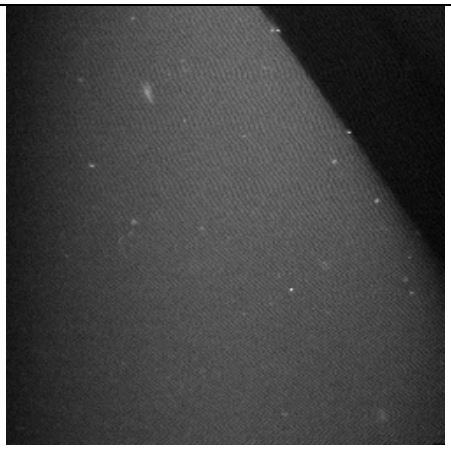


Figure S5:

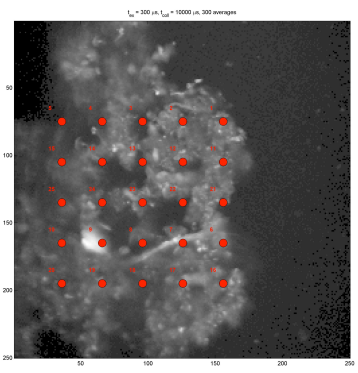


(a) Camera image through eyepiece of the custom-designed multimodal imaging system of visible aggregate and supernatant at pH 5 (0.18 mM) before addition of the first aliquot of HSA solution.

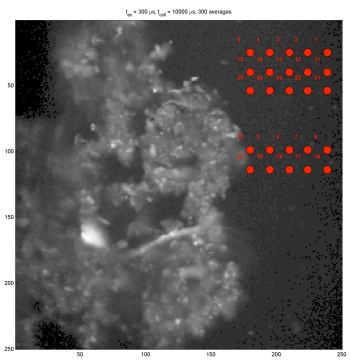


(b) Survey scan of **Eu-bbu** at pH 5 (0.18 mM) after the addition of the first aliquot of HSA solution ([HSA]=0.023 mM ; HSA :Eu-bbu = 0.13). Visible aggregate disappears with first addition of HSA.

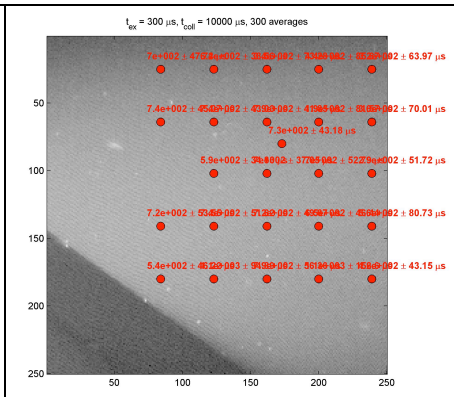
Figure S6 :



(a) **Eu-bbu** at pH5 (0.18 mM) containing no HSA. Red dots indicate selected points in the aggregate for luminescence lifetime measurements.



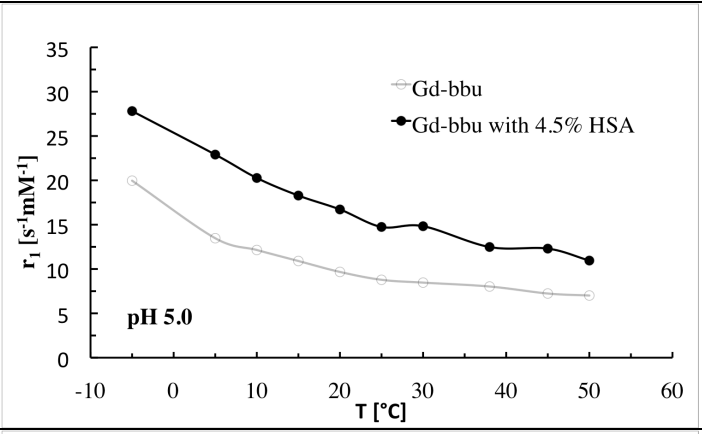
(b) **Eu-bbu** at pH5 (0.18 mM) containing no HSA. Red dots indicate selected points in the supernatant for luminescence lifetime measurements.



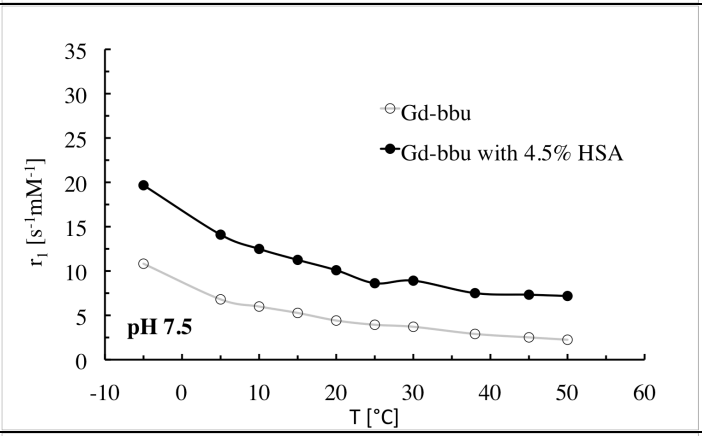
(c) **Eu-bbu** at pH5 (0.18 mM) with HSA (0.023 mM ; HSA :Eu-bbu = 0.13) with selected points for luminescence lifetime measurements.

Figure S7: Temperature dependence of relaxivity r_1 [$mM^{-1}s^{-1}$] of **Gd-bbu** with (filled symbols) and without 4.5% (w/v) HSA (open symbols) at pH 5 (a), pH 7.5 (b) and pH 8.5 (c).

(a)



(b)



(c)